UNIVERSITÉ DU QUÉBEC À MONTRÉAL

LES ÉMISSIONS DE DIOXYDE DE CARBONE (CO_2) ET DE MÉTHANE (CH_4) PROVENANT DES RÉSEAUX FLUVIAUX BORÉAUX: ESTIMÉS RÉGIONAUX ACTUELS ET RÉPONSE FUTURE FACE AUX CHANGEMENTS CLIMATIQUES

MÉMOIRE

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AVANT-PROPOS

Ce mémoire est séparé en quatre sections comprenant une introduction, suivie de deux chapitres sous forme d'articles scientifiques et une conclusion générale. L'introduction a pour but de faire un survol des connaissances scientifiques actuelles et mettre en contexte les objectifs et hypothèses adressés. Le premier chapitre de la thèse porte sur la contribution, des émissions de dioxyde de carbone (CO_2) et de méthane (CH_4) provenant des rivières et ruisseaux à l'échelle régionale dans un paysage boréale du Québec. Cet fut soumis à la revue scientifique *Global Biogeochemical Cycle* de l'American Geophysical Union. Le second chapitre porte sur la détermination et la quantification de l'impact potentiel des changements climatiques sur ces émissions fluviales de gaz à effet de serre. Cet article fut soumis à la revue scientifique *Global Change Biology*. Les deux articles scientifiques ont été rédigés en anglais dans la perspective d'une publication éminente. La conclusion a pour objectif de présenter un sommaire de la contribution du mémoire au savoir scientifique actuel.

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C	Carbone
CH_4	Méthane
CO	Carbone organique
CO_2	Dioxyde de carbone
COD	Carbone organique dissous
f_{CH4}	Flux de méthane
f_{CO2}	Flux de dioxyde de carbone
fD_{CH4}	Flux diffusif de méthane
GES	Gaz à effet de serre
Gg	Gigagramme (10^9 g)
k	Constante de Vitesse d'échange gazeux
k_{600}	Vitesse d'échange gazeux au nombre de Schmidt 600
kCH_4	Vitesse d'échange du méthane
kCO_2	Vitesse d'échange du dioxyde de carbone
Kh	Constante de Henry
pCH_4	Pression partielle du méthane
pCO_2	Pression partielle du dioxyde de carbone
Pg	Petagramme (10^{15} g)
Sc	Nombre de Schmidt
t	Tonne (10^6 g)
Tg	Teragramme (10^{12} g)
TSL	« *total stream length* » en anglais; Longueur total des ruisseaux en amont

RÉSUMÉ

Les rivières et ruisseaux, particulièrement dans la zone boréale, sont reconnus comme étant des sources importantes de dioxyde de carbone (CO_2) vers l'atmosphère. Toutefois, leur contribution aux émissions de méthane (CH_4) a été peu explorée et la sensibilité de ces émissions fluviales de gaz à effet de serre (GES) face aux changements climatiques n'a pas encore été déterminée. Dans cette étude, nous quantifions les émissions fluviales de CO_2 et de CH_4 à l'échelle régionale dans deux régions de la plaine boréale québécoise. Nous explorons par la suite la réaction potentielle de ces émissions face à divers scénarios prédits de changements climatiques. Toutes les rivières étaient largement sursaturées en CO_2 (de 1.5 à 33 fois) et en CH_4 (de 13 à 16 000 fois) par rapport à l'atmosphère et les émissions de CH_4 contribuaient à 33% des émissions annuelles de GES. Des modèles empiriques régionaux ont par la suite démontré que l'augmentation prédite de température et de vélocité de l'eau, ainsi que de la concentration en carbone organique dissout (COD), pourront mener à une augmentation significative des émissions fluviale de GES, principalement causée par une hausse marquée des émissions de CH_4. Contrairement aux paradigmes actuels, nous avons démontré que les réseaux fluviaux de la zone boréale agissent comme des sources importantes de CH_4 vers l'atmosphère, lesquelles risquent d'être amplifiées sous l'effet du réchauffement climatique global.

Mots clés : Dioxyde de carbone, méthane, gaz à effets de serre, concentration, flux, émission, rivières, ruisseaux, réseaux fluviaux, réchauffement et changements climatiques.

INTRODUCTION

0.1 Le cycle biogéochimique du carbone

Le dioxyde de carbone (CO_2) et le méthane (CH_4) sont deux gaz à effet de serre (GES) puissants, dont la concentration atmosphérique croissante menace l'équilibre climatique actuel (Solomon *et al.*, 2007). Ce phénomène résulte en directement des activités anthropiques, mais est aussi largement modulée par des mécanismes naturels, englobés sous le titre du cycle biogéochimique du carbone (C). Par divers processus de transfert, d'échange et de transformation, le cycle biogéochimique du C parvient aujourd'hui à tamponner près de 54% [5 Pg de C] du CO_2 atmosphérique largué dans l'atmosphère par les activités anthropiques tout en contribuant à près de 45% [230 Tg de C] du CH_4 libéré annuellement dans l'atmosphère (Canadell *et al.*, 2007, Denman *et al.*, 2007). Ainsi, notre capacité à comprendre et à prédire la concentration atmosphérique de gaz à effet de serre, dans un contexte d'instabilité climatique, repose en grande partie sur notre compréhension de ces processus naturels associés au cycle biogéochimique du C.

Une partie dominante de ces processus naturels s'effectue à la surface des continents, notamment via l'activité photosynthétique des forêts, puisant annuellement près de 2.8 Pg de C du CO_2 atmosphérique à l'échelle des continents (Canadell *et al.*, 2007, Solomon *et al.*, 2007) ainsi que par la décomposition bactérienne dans les milieux humides, libérant vers l'atmosphère près de 200 Tg de C sous forme de CH_4 (Cicerone & Oremland, 1988, Denman *et al.*, 2007). Dans les

régions de haute latitude comme le biome boréal, ces deux mécanismes prennent une ampleur considérable puisque ces régions renferment à la fois la plus large étendue forestière au monde ainsi qu'une densité inégalée de zones humides. Ainsi, le biome boréal est reconnu pour jouer un rôle prépondérant dans la modulation des concentrations atmosphériques des deux gaz à effet de serre, CO_2 et CH_4 (Chapin *et al.*, 2000, Dixon, 1994, Dlugokencky *et al.*, 1994, Gorham, 1991).

Le biome boréal est également un acteur important dans le système climatique puisqu'il renferme la plus dense réserve mondiale de C [471 Pg de C], emmagasinée sous formes organiques et inorganiques dans ces sols et tourbières (Dixon, 1994, Gorham, 1991). Au cours de l'infiltration et de l'écoulement de l'eau de pluie dans les sols, les eaux souterraines s'enrichies en C organique, inorganique et gazeux (CO_2 et CH_4) et sont déversé vers les lacs, rivières et ruisseaux. Ce mode de transfert latérale de C résulte en une perte chronique de C d'origine terrestre (Meybeck, 1993, Worrall & Lancaster, 2005). De par cette voie d'échange carbonique entre le milieu aquatique et terrestre, les écosystèmes aquatiques ont été décrits comme des sources de gaz carbonique envers l'atmosphère. De récentes études ont d'ailleurs démontré que ces émissions pourraient atteindre des ordres de magnitudes semblables à ceux de processus depuis longtemps pris en compte dans le paysage boréal tel que l'absorption de CO_2 par les forêts, le transport de C organique terrestre vers les océans et la séquestration de C dans les sols et tourbières (Cole *et al.*, 2007, Cole & Caraco, 2001, Tranvik *et al.*, 2009).

0.2 Rôle des écosystèmes aquatiques dans le cycle du C

Dans le biome boréal, les écosystèmes d'eaux douces couvrent de 10 à 30% de la surface du paysage, l'une des densités les plus importantes au monde. On attribue aujourd'hui deux rôles majeurs aux écosystèmes aquatiques dans le paysage boréal, 1) la fonction de conduit permettant le transfert du CO_2 et du CH_4 emprisonnés dans les sols vers l'atmosphère (Fiedler *et al.*, 2006, Oquist *et al.*, 2009, Worrall & Lancaster, 2005) et 2) la fonction de réacteurs produisant eux-mêmes du CO_2 et du CH_4 par la dégradation du C organique lessivé du milieu terrestre (Battin *et al.*, 2008, Cole & Caraco, 2001, Richey *et al.*, 2002). L'action simultanée de ces deux mécanismes, résultent en des taux considérablement élevé d'émission de gaz carbonique venant des écosystèmes d'eaux douces (Butman & Raymond, 2011, Cole *et al.*, 2007, Tranvik *et al.*, 2009).

Les lacs occupent une partie dominante au sein du couvert aquatique boréal, alors que les rivières et les ruisseaux n'occupent rarement plus de 5% du territoire aquatique. Pour cette raison, les rivières et les ruisseaux ont longtemps été perçus comme des émetteurs de gaz carbonique négligeables, aux côtés des lacs qui ont reçus jusqu'à maintenant beaucoup plus d'attention. Cette perception a récemment été contestée puisque de récentes études ont démontré que les flux de CO_2 vers l'atmosphère, provenant des rivières et ruisseaux, sont largement supérieurs à ceux des lacs. Par conséquent, les systèmes fluviaux agissent comme des points chauds d'émission de CO_2 dans le réseau aquatique, pouvant contribuer jusqu'à 65% des

émissions aquatiques totales à l'échelle régionale (Humborg *et al.*, 2010, Jonsson *et al.*, 2007, Teodoru *et al.*, 2009).

Ces émissions disproportionnément importantes de CO_2 surviennent à la fois de la profonde interconnexion des rivières et ruisseaux avec le milieu terrestre, agissant comme des conduits rapides de gaz carbonique dérivé des sols vers l'atmosphère, mais aussi de leur apport considérable en C organique terrestre, permettant des taux de production de gaz carbonique élevés (Aufdenkampe *et al.*, 2011, Battin *et al.*, 2008). Malgré ce changement drastique de perception, les systèmes fluviaux (rivières et ruisseaux) sont encore perçus comme des sources négligeables de CH_4 atmosphérique, par opposition aux lacs, étangs et tourbières qui ont, depuis les dernières décennies, reçu un intérêt considérable (Bastviken *et al.*, 2011, Roulet *et al.*, 1992b, Teodoru *et al.*, 2012). Cette conception repose toutefois sur un nombre très restreint d'observations, limitant aujourd'hui notre capacité de comprendre le rôle des rivières et ruisseaux au sein de la balance de GES du biome boréal.

Malgré la faible représentativité des rivières et ruisseaux dans les estimés mondiaux et boréaux actuels de CH_4, il nous est tout de même possible d'observer que ces systèmes semblent systématiquement sursaturés en CH_4 par rapport à l'atmosphère à l'échelle globale (Baker *et al.*, 1994, Dahm *et al.*, 1991, Hope *et al.*, 2004), et donc agiraient comme des sources de CH_4 vers l'atmosphère, sans toutefois que ces émissions n'aient pu être quantifiées de façon élaboré jusqu'à maintenant (Bastviken *et al.*, 2011). Dans le biome boréal, les rivières et ruisseaux drainent de

vastes étendues de tourbières, parsemées de zones humides et sont également fortement affectés par les barrages de castors. Ces deux écosystèmes sont reconnus comme des sources fondamentale de CH_4 atmosphérique (Ford & Naiman, 1988, Roulet *et al.*, 1992b, Weyhenmeyer, 1999), qui pourrait potentiellement favoriser un apport substantiel de CH_4 dans les réseaux fluviaux boréaux (Billett & Harvey, 2012, Billett & Moore, 2008). De ce fait, il devient clair qu'un effort considérable doit être effectué afin de mieux caractériser et quantifier les émissions fluviales de CH_4, spécialement dans le paysage boréal, qui jusqu'à aujourd'hui, demeurent peu explorées et inquantifiées.

0.3 Quantifier les émissions fluviales de GES

De par le rôle prépondérant que semble occuper les rivières et ruisseaux dans le cycle biogéochimique du C, un intérêt grandissant pour développer une meilleure compréhension et quantification des émissions fluviales de GES se développe auprès de la communauté scientifique (Aufdenkampe *et al.*, 2011, Battin *et al.*, 2008, Butman & Raymond, 2011). Jusqu'à aujourd'hui, la dynamique du C dans les écosystèmes fluviaux fut typiquement étudiée à une échelle spatiale restreinte, celle du bassin versant ou du continuum de rivière. Cette approche nous procure désormais un aperçu fragmenté des émissions fluviales de CO_2 et CH_4 dans le territoire, mais qui se présente aujourd'hui comme l'unique option offerte permettant d'extrapoler ces émissions à l'ensemble du biome boréal et même du globe (Aufdenkampe *et al.*, 2011, Bastviken *et al.*, 2011). Cette approche limite également notre compréhension

des liens existant entre les propriétés du paysage boréal et la dynamique des GES dans les rivières, mais diminue aussi la fiabilité des estimés à large échelle. Il nous faut donc développer de nouvelles approches qui permettront de faire le pont entre ces études à faible résolution spatiale et les estimés globaux, de manière à acquérir une vision plus compréhensive et adéquate du rôle des écosystèmes fluviaux dans le cycle biogéochimique du C. Une façon de parvenir à cette tâche serait de déployer des études à une échelle spatiale plus vaste, ce qui permettrait d'intégrer l'hétérogénéité naturelle du paysage boréal et d'identifier les éléments du paysage qui influencent de façon plus importante les flux de gaz carbonique des réseaux fluviaux.

Les flux diffusifs de gaz carbonique entre l'atmosphère et les eaux de surface des rivières sont dictés à la fois par la pression partielle de CO_2 et CH_4 (pCO_2 et pCH_4) (µatm) dans les eaux de surface ainsi que par le coefficient d'échange gazeux (k) (m d^{-1}), lequel exprime la vitesse d'équilibration entre l'eau de surface avec l'atmosphère subjacent. Ces deux variables sont contrôlées par des propriétés environnementales distinctes, et ainsi semblent varier spatialement et saisonnièrement suivant des patrons alternatifs. La pression partielle de CO_2 et de CH_4 (pCO_2 et pCH_4) dans les eaux de surface des rivières et des ruisseaux se situe typiquement bien au-delà des concentrations atmosphériques, menant à une pression de diffusion du gaz vers l'atmosphère (Bastviken *et al.*, 2011, Del Giorgio *et al.*, 1997, Duarte & Prairie, 2005). Le degré de sursaturation en CO_2 et CH_4 dans les rivières et ruisseaux est toutefois très variable, suivant par exemple; les patrons hydrologiques dans le bassin versant et le réseau fluvial (Jones & Mulholland, 1998a, Oquist *et al.*, 2009,

Wallin *et al.*, 2010), l'abondance de tourbières, de zones humides et de forêts dans le bassin versant, (Billett & Moore, 2008, Sobek *et al.*, 2003, Wallin *et al.*, 2010), et aussi selon l'activité métabolique dans le milieu fluvial (Dahm *et al.*, 1991, Dawson *et al.*, 2001, Richey *et al.*, 1988).

Le coefficient d'échange gazeux (k), est majoritairement contrôlé par la turbulence de l'eau dans les systèmes d'eau courante (Macintyre *et al.*, 1995, Vachon *et al.*, 2010, Wallin *et al.*, 2011), et varie donc aussi temporellement, selon l'écoulement saisonnier et spatialement selon l'hydrologie entre divers systèmes ou l'alternance de fosses et de rapides au sein d'un même ruisseau (Wallin *et al.*, 2011). La variabilité naturelle de ces deux paramètres, pCO_2-pCH_4 et k, entrave les possibilités et la fiabilité des extrapolations d'étude à faible résolution spatiale et temporelle, vers des budgets annuelles et de large échelle des émissions de GES provenant des réseaux fluviaux. C'est pourquoi il devient nécessaire de développer notre compréhension de ces divers aspects à l'échelle régionale, nous permettant ainsi d'extraire des patrons de la pCO_2, de la pCH_4 et du k intégratif de l'hétérogénéité spatiale du paysage et temporelle des saisons. Il deviendra aussi essentiel de baser ces patrons sur des variables facilement quantifiables à grande échelle spatiale, afin de nous permettre d'extrapoler avec précision les émissions fluviales de GES dans le biome boréal.

0.4 Représentativité actuelle du biome boréal

Le biome boréal est le plus vaste biome terrestre au monde et de ce fait, comprend une géologie et un couvert forestier très contrasté d'une région à une autre. Ce biome est aussi relativement peu exploré par rapport à d'autres; tels que le biome tempéré ou tropical, puisqu'il est en général très peu habité. Jusqu'à maintenant, la majeure partie des études portant sur la dynamique des GES dans les réseaux fluviaux boréaux a été conduite en Scandinavie ou en Alaska, là où l'on retrouve une plus forte population (Humborg *et al.*, 2010, Huttunen *et al.*, 2003, Kling *et al.*, 1992). Nos connaissances sont majoritairement restreintes à ces deux régions, limitant ainsi notre compréhension de la dynamique GES dans les réseaux fluviaux pour l'ensemble du paysage boréal. En fait, ces régions abordent des paysages particuliers, n'étant pas nécessairement représentatifs de l'ensemble du biome boréal. On y retrouve notamment une topographie accidentée qui contraste fortement avec les vastes plaines boréales retrouvées dans le Bouclier Canadien et en Sibérie (Turetsky *et al.*, 2005).

Les plaines boréales ont été façonnées par la déglaciation massive de l'hémisphère nord à la fin de l'Holocène, laquelle ayant permis l'implantation de gigantesques lacs glaciaires qui ont modelé l'ensemble du paysage actuel (Terasmae & Hughes, 1960). Ces régions renferment les plus denses étendues de tourbières et de zones humides du biome boréal (Gorham, 1991, Tremblay *et al.*, 2002), lesquelles sont reconnue comme des sources importantes de GES vers l'atmosphère et envers les eaux souterraines se déversant dans les rivières et ruisseaux (Billett & Moore,

2008, Dinsmore *et al.*, 2009, Hope *et al.*, 2001). Le relief est également un facteur-clé modulant l'infiltration et l'écoulement de l'eau de pluie dans le territoire (McGuire *et al.*, 2005, Tetzlaff *et al.*, 2011) et pourrait de ce fait affecter le transferts latérale de C terrestre dans le milieu aquatique (Hamilton *et al.*, 1994, Mulholland, 1981, Ullah & Moore, 2011). L'influence de la topographie sur l'hydrologie pourrait également avoir un impacte sur la vitesse d'échange gazeux entre l'atmosphère et les eaux de surface (k) au sein des rivières et des ruisseaux (Macintyre *et al.*, 1995, Wallin *et al.*, 2011), ainsi que sur les propriétés biophysiques permettant la dégradation du C organique terrestre dans le réseau fluvial (Battin *et al.*, 2008, Hlavacova *et al.*, 2006). Les régions de plaines semblent donc renfermer des propriétés géologiques et hydrologiques qui pourraient influencer l'approvisionnement et la production aquatique de GES dans les réseaux fluviaux et son évasion subséquente vers l'atmosphère.

La faible représentativité actuelle des régions de faible topographie dans les études portant sur la dynamique des gaz carboniques dans les réseaux fluviaux pourrait donc imposer des biais importants quant à notre compréhension actuelle des patrons de pCO_2, pCH_4 et k dans les rivières et ruisseaux. Compte tenu de l'impact potentiellement important de la topographie sur la fonction de conduit et réacteur de CO_2 et CH_4 dans les rivières et ruisseaux, ainsi que sur la physique des échanges gazeux entre les eaux de surface et l'atmosphère, il apparait judicieux de tenter de caractériser les émissions fluviales de GES dans ces régions de faible relief, jusqu'à aujourd'hui peu étudiées.

0.5 Émissions de GES lors du dégel printanier

La saison hivernale occupe plus de la moitié du cycle annuel dans le biome boréal et a longtemps été considérée comme une période biologiquement inerte où l'activité métabolique bactérienne est largement ralentie par les basses températures. Ainsi, il fut longtemps assumé que les périodes hivernales contribuent peu au budget annuel de GES dans le biome boréal. Des récentes études ont contredit cette perception, en démontrant que les concentrations de gaz carbonique sous la glace excède parfois les concentrations annuelles moyennes dans les lacs nordiques (Demarty *et al.*, 2011, Kortelainen *et al.*, 2006, Michmerhuizen *et al.*, 1996). Ces hautes concentrations hivernales résulteraient de l'accumulation progressive des gaz carboniques sous le couvert de glace, limitant les échanges gazeux entre l'atmosphère et les eaux de surface et agissant ainsi comme une couche isolante à la surface des lacs. Il s'en suivrait donc une libération massive de gaz carboniques lors du dégel printanier, pouvant contribuer jusqu'à 53% des émissions annuelles de GES durant cette courte période (Algesten *et al.*, 2004, Demarty *et al.*, 2011, Huotari *et al.*, 2009). Dus à des contraintes d'ordre logistique, ces aspects de la dynamique annuelle des GES demeurent inexplorés dans les réseaux fluviaux, mais pourraient de façon similaire contribuer aux estimés annuelles des émissions fluviales de GES. Il nous faut donc explorer la dynamique des processus hydrologiques et biologiques prenant place lors de la fonte printanière dans les rivières de la zone boréale, afin de quantifier les émissions de GES produites durant cette période critique de l'année.

Ceci, afin de nous d'améliorer la fiabilité des budgets annuels d'émissions aquatique de GES.

0.6 Réponse potentielle face aux changements climatiques

Les effets prédits des changements climatiques à venir seront intensifiés dans le biome boréal (Flato & Boer, 2001, Friedlingstein & Prentice, 2010, Scinocca *et al.*, 2008), motivant ainsi plusieurs chercheurs à tenter de prédire l'effet potentielle de ces changements sur le cycle biogéochimique du carbone dans les régions boréales (Bonan, 2008, Chapin *et al.*, 2000, Goodale *et al.*, 2002). Ces études ont jusqu'à maintenant permis de démontrer que les processus actuels régissant le cycle du C au sein du biome boréal, par exemple dans les forêts (Bonan, 2008, Bond-Lamberty *et al.*, 2007, Keyser *et al.*, 2000), sols et tourbières (Davidson & Janssens, 2006, Gorham, 1991, Goulden *et al.*, 1998), et lacs (Benoy *et al.*, 2007, Gudasz *et al.*, 2010, Schindler *et al.*, 1996) sont excessivement sensibles aux changements prédit de température, de précipitations et d'écoulements résultant du réchauffement globale.

Puisque le rôle, étonnamment important, des rivières et des ruisseaux en tant qu'émetteurs de gaz carboniques dans le paysage boréal n'a été que tout récemment démontré, leurs réponses potentielles face aux changements climatiques n'ont encore été peu explorées. Néanmoins, il est possible de constater que les changements environnementaux prédits par les scénarios de changements climatiques influenceront les propriétés hydrologiques, thermiques et biophysiques des rivières (Benoy *et al.*, 2007, Clair *et al.*, 1998, Köhler *et al.*, 2009), et ainsi suggère d'avoir une influence

importante sur l'approvisionnement, la production et les émissions GES des réseaux fluviaux boréaux. Il apparait donc judicieux de déterminer comment les concentrations en gaz carbonique des rivières (pCO_2 et pCH_4), ainsi que le coefficient d'échange gazeux (k), seront affectés par ces changements anticipés des propriétés des rivières, et par la même occasion, de déterminer le rôle futur qu'assumeront les rivières et ruisseaux dans un contexte d'instabilité climatique.

0.7 Objectifs et hypothèses

Conformément à l'état des connaissances actuelles, nous avons pu constater que les réseaux fluviaux occupent une place prépondérante dans le cycle du C, mais que plusieurs concepts manquants limitent notre compréhension de l'importance des émissions fluviales de GES. Notamment, concernant l'ampleur des émissions fluviales de CH_4 dans la zone boréale, on constate également la rareté des études à l'échelle régionale portant sur les émissions fluviales de GES, la faible représentativité des réseaux fluviaux des régions de faible relief, la méconnaissance de l'importance des émissions fluviales de GES lors du dégel printanier et l'inaptitude à déterminer la réponse potentielle de émissions fluviales de GES face aux changements climatiques.

Ce mémoire vise donc à 1) explorer les patrons de concentrations et flux de CO_2 et CH_4 provenant des réseaux fluviaux boréaux dans une régions de faible topographie 2) quantifier à l'échelle régionale les émissions fluviales de GES au cours d'une année complète (incluant la période critique du dégel printanier) et

déterminer leur importance dans le paysage boréal 3) déterminer la réponse potentielle des émissions fluviales de GES aux changements climatiques. Afin de répondre à ces objectifs, j'ai effectué un échantillonnage à l'échelle régionale des concentrations et des flux de CO_2 et de CH_4 provenant des réseaux fluviaux au cours d'une année complète, incorporant chacune des gammes de tailles de rivières et ruisseaux présentes dans deux régions situées au Nord du Québec, l'Abitibi et la Baie James. Ces deux régions abordent un paysage contrasté par le type de sol et l'abondance de tourbières, mais abordent toutes deux un climat continental humide similaire et une faible topographie.

Je souhaite de ce fait contribuer à bâtir une image plus complète de l'importance des émissions fluviales de GES dans la zone boréale. Je testerai l'hypothèse que les émissions fluviales de CH_4, tout comme il le fut ultérieurement démontré pour les émissions de CO_2, seront disproportionnément importantes dans le paysage boréal pour ces deux régions de faible topographie. Je crois que la faible topographie aura pour effet d'amplifier la sursaturation de CO_2 et de CH_4 dans les eaux de surface du réseau fluvial et dévoilera ainsi des patrons de pCO_2, pCH_4 et de k encore peu documentés dans la zone boréale. Je testerai également l'hypothèse que les changements climatiques anticipés pour ces deux régions auront pour effet d'amplifier les émissions actuelles de GES dans le réseau fluvial. Je crois qu'une augmentation de température et de concentration de DOC favorisera l'augmentation de la pCO_2 et pCH_4 dans le réseau fluvial alors que l'augmentation des débits et de l'écoulement accentuera les échanges gazeux avec l'atmosphère.

CHAPITRE I

REGIONAL CONTRIBUTION OF CO_2 AND CH_4 FLUXES FROM THE FLUVIAL NETWORK IN A LOWLAND BOREAL LANDSCAPE OF QUÉBEC

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1.2 Abstract

Boreal rivers and streams are increasingly recognized as significant sources of atmospheric CO_2, but their role as CH_4 emitters is considered relatively negligible. This assumption is based on a few and spatially fragmented data. In this context, this study explores the regional scale patterns in river greenhouse gas concentration (CO_2 and CH_4) and gas exchange coefficient (k_{600}) in a lowland boreal region of Northern Québec, and to further combine these models to estimate the total CO_2 and CH_4 emissions for the entire fluvial network in this region. Our results show that these lowland fluvial networks are largely supersaturated in both gases, with pCO_2 and pCH_4 declining with increasing river size. On the contrary, the k_{600} tended to increase with stream order, which may be characteristic of the stream hydrology in this flat landscape. Nonetheless, the smallest streams (order 1), which represent < 20% of the total river surface, contributed over 30% of the total fluvial GHG emissions. The end of winter and the spring thaw periods, which are rarely included in annual emission budgets, also contributed on average 19% of the annual GHG emissions. As a whole, the fluvial network released on average 1.7 tons of C (CO_2 eq.) yr^{-1} km^{-2} of landscape, of which CH_4 emissions contributed approximately 33% (in CO_2 eq.). Fluvial CH_4 emissions could represent between 36 to 60% of the total aquatic (lakes, reservoirs and rivers) CH_4 emissions in the region, despite the relatively small riverine surface (4.3% of the total aquatic surface). We conclude that fluvial networks in these boreal lowlands play a disproportionately large role as hot spots for CO_2 and more unexpectedly as CH_4 emissions as well, which cannot be ignored in large-scale GHG budgets for boreal landscapes.

1.3 Introduction

The boreal biome contains one of the world's highest densities of inland waters (comprising 10-30% of the total area), which are now increasingly recognized as significant players in the overall carbon (C) and greenhouse gas (GHG) (CO_2 and CH_4) balance of this biome (Bastviken *et al.*, 2011, Cole *et al.*, 2007, Tranvik *et al.*, 2009). Over the past decade, it has become apparent that CO_2 emissions from boreal lakes and rivers are of the same magnitude as the C export to the sea (Aufdenkampe *et al.*, 2011, Striegl *et al.*, 2012, Tranvik *et al.*, 2009) and the landscape net ecosystem exchange (Fiedler *et al.*, 2006, Jonsson *et al.*, 2007).

Our understanding of the magnitude of CH_4 emissions from boreal aquatic ecosystems has lagged well behind that of CO_2. A recent meta-analysis of existing data concluded that CH_4 emissions from boreal inland waters (lakes, rivers and reservoirs but excluding wetlands) could be in the order of 8 Tg CH_4 yr^{-1} (Bastviken *et al.*, 2011); in the same magnitudes as the total CH_4 emissions from the northern wetlands (in the range of 30-40 Tg CH_4 yr^{-1}](Bartlett & Harriss, 1993), which are considered as one of the largest source of CH_4. These large-scale aquatic CH_4 emission estimates are based on few and extremely fragmented data, but are also biased in terms of the types of systems covered. Up to present, research on boreal CH_4 emissions has focused mainly on wetlands (Macdonald *et al.*, 1998, Roulet *et al.*, 1992a, Whiting & Chanton, 2001), and to a much lesser extent, on lakes (Bastviken *et al.*, 2004, Bastviken *et al.*, 2011) and reservoirs (Duchemin *et al.*, 1995, Teodoru *et al.*, 2012). A major gap in these regional aquatic CH_4 budgets is the almost complete

absence of information on the potential contribution of flowing waters (Bastviken *et al.*, 2011).

Streams and rivers have traditionally been viewed as conduits for terrestrially-produced CO_2 to the atmosphere (Fiedler *et al.*, 2006, Oquist *et al.*, 2009, Worrall & Lancaster, 2005), but they are also increasingly recognized as reactors processing large amounts of organic carbon leaching from terrestrial ecosystems, and thus significant generators of CO_2 (Battin *et al.*, 2008, Cole & Caraco, 2001, Richey *et al.*, 2002). The combined result of these two functions (the conduit and the reactor) are extremely high CO_2 fluxes, and it has been recently estimated that streams and rivers may contribute up to 65% to the total aquatic CO_2 emissions, while accounting for less than 5% of the total aquatic surface (Humborg *et al.*, 2010, Jonsson *et al.*, 2007, Teodoru *et al.*, 2009). This in turn has motivated increased efforts to more accurately estimate CO_2 emissions from rivers and streams at regional and continental scales (Aufdenkampe *et al.*, 2011, Butman & Raymond, 2011, Humborg *et al.*, 2010).

Contrary to their role in CO_2 dynamics, streams and rivers have never been considered significant sites for CH_4 emission, partly due to their small relative surface coverage, and also due to the perception that running waters do not provide conditions for significant methane production. There is evidence, however, that these assumptions are unfounded: Streams have been shown to act as conduits for significant fluxes of terrestrially-produced CH_4 to the atmosphere as they are for CO_2 (Crawford *et al.*, 2013, Hope *et al.*, 2004, Jones & Mulholland, 1998b). In addition, methane production has been documented in various types of rivers (Jones *et al.*, 1995, Richey

et al., 1988, Roulet *et al.*, 1997). For example, it has been estimated that up to 20% of the carbon mineralization in rivers could occur in anoxic areas and result in CH_4 evasion to the atmosphere (Richey *et al.*, 1988). In addition, stream and river beds have been shown to be sources of significant amounts of CH_4 that may be emitted to the atmosphere via macro-bubble release (Baulch *et al.*, 2011). While this fragmented evidence suggests that streams and rivers may potentially be sites of significant CH_4 emissions, the paucity of published measurements on stream CH_4 emissions do not allow to assess the importance of CH_4 emissions at regional or even watershed scales. This is particularly problematic in northern landscapes, which are characterized by extensive and complex river networks.

Here we present a large-scale, comparative study of CH_4 and CO_2 concentration and emissions from the fluvial network in the Abitibi and James Bay regions of boreal Québec. These regions represent a distinct landscape type within the boreal biome that is widespread across North America and the Siberian Plateau, and which is characterized by a very flat topography, clay-dominated deposits, and dominance of peat-bogs in the case of the James Bay region. In a companion paper, we explore the drivers of these fluxes and their connections to river and watershed properties. In the component that we present here we focus on the scaling of the resulting fluxes and assessing their relative importance at the regional level. The fluvial network in this boreal landscape is complex and composed of rivers that range orders of magnitude in size and discharge, and watershed properties. In order to upscale measured fluxes to the whole region, we first need to develop empirical

models that allow us to estimate gas concentrations and exchange on the basis of easily quantifiable properties that span the range of these stream and river types. We have thus, sampled the whole spectrum of stream orders present in the region, and have developed empirical models to predict ambient river CO_2 and CH_4 partial pressure (pCO_2 and pCH_4, respectively) and their gas exchange rates (k) on the basis of stream properties that can be easily extrapolated and determined geographically. We also gave special attention to winter and spring CO_2 and CH_4 dynamics in a subset of our rivers, and we have used the observed patterns to estimate spring thaw gas fluxes at the regional scale, which is possibly a crucial period, rarely included in annual budgets. We combined the resulting regional models of ambient gas concentrations and of gas exchange with detailed geographical analysis of the fluvial network, to derive the actual CO_2 and CH_4 emissions from the ensemble of rivers in the region.

1.4 Material and Methods

1.4.1 Study region and sampling design

We sampled rivers and streams located in the boreal mixed forest of Québec, Canada, within two distinct regions: The Abitibi (47-48°N, 78-79°W), and The James Bay (48-49°N, 78-79°W) (Figure 1.1). These two regions are marginal landforms created by the retreat of the Laurentian ice sheet that formed a large plain (average elevation of 300 m ± 31SD) of glacio-fluvial sediments rich in till and clay and organic deposits (Veillette *et al.*, 2008). The regions differ from each other in terms of their plant cover and dominant surface soil deposit type, and the configuration of their aquatic network, whereas large lakes dominate the Abitibi region and small lakes and wetlands dominate the James Bay region (Table 1). The fluvial network in both regions is extensive and forms a trellis and dentritic drainage pattern, with systems ranging from up to 6 Strahler stream order. The low order streams (1 to 3) in the Abitibi region are intensively affected by beaver, which strongly influence the hydrological regime (Naiman *et al.*, 1988). However, beaver impoundments are almost non-existent in the James Bay region due to the sparse coverage of broadleaf forests.

We have surveyed 46 different streams and rivers between May 2010 and May 2011, from which 31 sites where located in the Abitibi region and 15 in the James Bay region (Figure 1.1). The streams and rivers were selected to include all the different stream orders present in each region and to be part of independent catchments for a

better representation of the regional landscape attributes. All 46 sites were visited once in mid-summer (July and August 2010) and 32 sites in early summer and in autumn (end of May and June 2010 and October 2010 respectively). In addition, a subset of 13 sites, restricted to the Abitibi region and covering the whole size spectrum were surveyed throughout the ice-covered and ice-breaking periods i.e. at the end of the winter (mid-March 2011), one week after the ice-break (mid-April 2011) and 4 weeks after the ice-break (early-May 2011). Recharge stream flows typically occur twice a year, once at spring thaw (April-May), and once in autumn (September-October) due to increased precipitation and overland flow. However, the summer of 2010, during which this study was carried out, was significantly dryer (50% less precipitations) than the long-term annual average, whereas autumn (September 2010) and spring (April 2011) received twice as much rain compared to annual averages (Table 1).

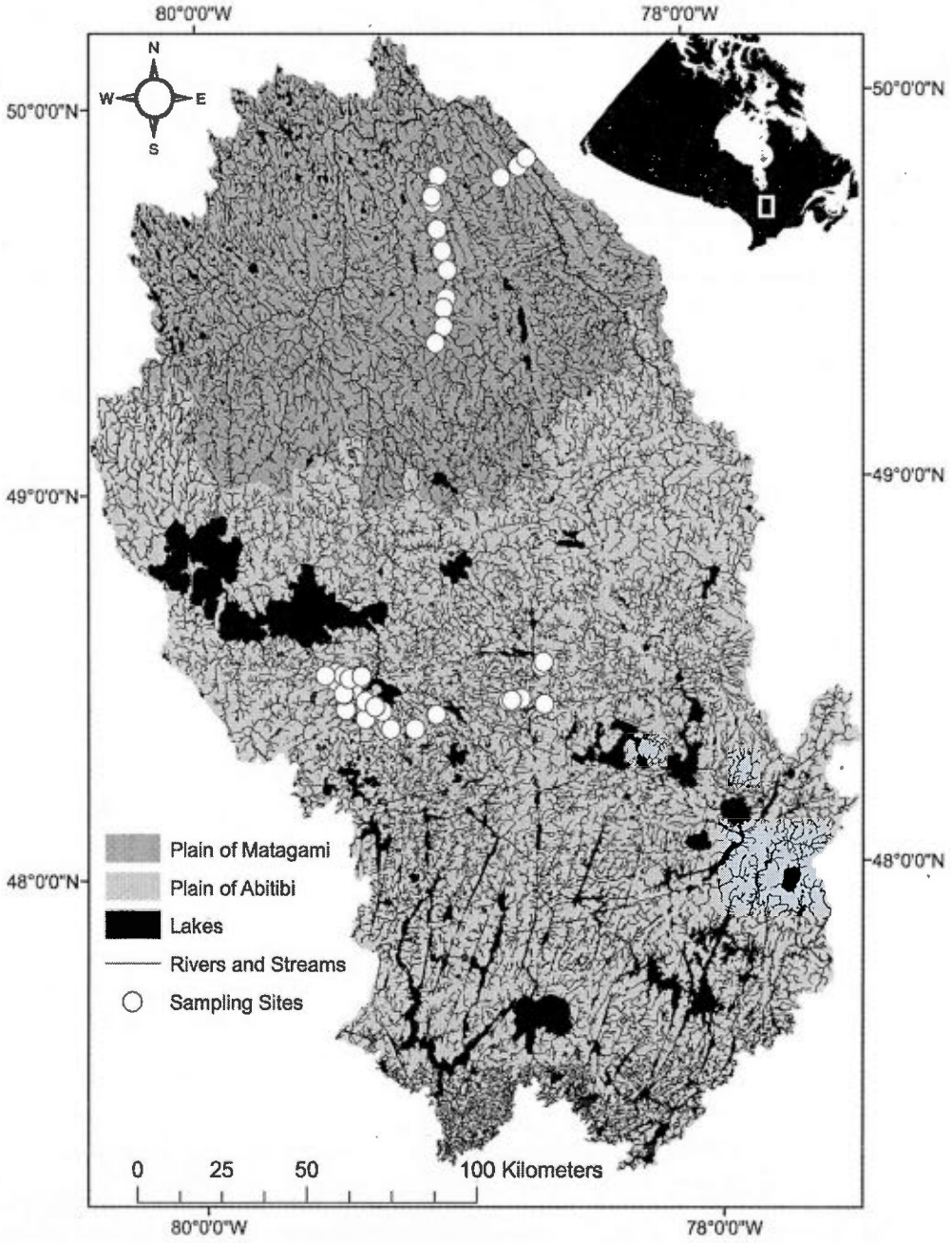

Figure 1.1: Map showing the distribution of sampled rivers and streams within the two studied regions, Abitibi and James Bay, and the delineation of the hydrological region, covering a total of 44 182km^2, for which we have estimated the annual fluvial CO_2 and CH_4 emission. This map also illustrates the extent of the aquatic coverage, which occupies a total of 9.3% of the territory.

Table 1.1: Landscape and climatic properties for the Abitibi and James Bay regions.

Region	Area (km^2)	Forested coverage	Dominant tree species	Dominant surficial soil deposit (%)	Inland water coverage (%)	Annual temperature (C°)	Annual precipitation
Abitibi	30 418	Coniferous (26%) Broadleaf (61%) Mixed wood (13%) Shrub land (10%)	balsam fir (*Abies balsamea*) white birch (*Betula papyrifera*) white spruce (*Picea glauca*) american aspen (*Populus tremuloides*)	Clay (50%) Till (25%) Roc (17%) Sand (4%).	Lakes (11%) Wetlands (3%) Fluvial (0.5%)	Average 0.7 Maximum 16.7 Minimum -17.9	Rain 700 mm Snow: 250 cm total 950 mm
James Bay	13 790	Coniferous (67%) Broadleaf (30%) Mixed wood (3%) Shrub land (11%)	black spruce (*Picea mariana*) Undergrowth: mosses (*Hypnaceae*) shrubs (*Ericaceae*)	Organic (95%) Clay (5%)	Lakes (3%) Wetlands (18%) Fluvial (0.4%)	Average -0.7 Maximum 16.0 Minimum -20.0	Rain 618 mm Snow 314 mm total 905 mm

1.4.2 Surface water pCO_2 and pCH_4 concentration

Our approach in this paper has been to quantify regional patterns in both surface water gas concentrations (pCO_2 and pCH_4), and in the gas transfer velocity (k), and to explore the environmental and climatic factors that shape these regional patterns. Fick's law of gas diffusion describes gas fluxes across the air-water interface, as follows:

$$f = k * Kh\ (pX_{water} - pX_{air}) \qquad (1.1)$$

where f is the gas flux at the interface air-water for a rather soluble gas, in our case CO_2 and CH_4, k is the gas transfer velocity (m d^{-1}) at a given temperature, Kh is the Henry's coefficient (adjusted for ambient salinity and temperature), and pX_{water} and pX_{air} are the partial pressures of the given gas in water and air, respectively. This equation shows that the diffusive fluxes are driven by both the gas oversaturation (ΔpX) in surface waters and the physical enhancement of the gas transfer velocity (k).

Surface water pCO_2 and pCH_4 were measured using the headspace equilibrium method. 60 ml polypropylene syringe were used to collect 30ml of stream water from approximately 10cm bellow the surface and added this volume to 30ml of ambient air to create a 1:1 ratio of ambient air: stream water. For pCO_2, triplicate syringes were vigorously shaken for 1 minute, in order to equilibrate the gases in water and air. The resulting headspace was directly injected into an infrared

gas analyzer (PP Systems, EGM-4). The original surface water pCO_2 was then calculated according to the headspace ratio and in situ measured ambient air pCO_2.

A similar procedure was used for collection of surface water pCH_4. The resulting 30 ml headspace, however, was rather injected into 30-ml glass vials equipped with rubber stoppers (20mm of diameters red bromobuptyl) filled with saturated saline solution (David Bastviken, personal communication), and kept upside-down until analysis. In the lab, the air stored in the vials was injected into a Shimadzu GC-8A Gas chromatograph with FID (flame ionization detector), to determine the CH_4 concentration in the sample. The original surface water pCH_4 was then calculated according to the headspace ratio and assuming a constant ambient air pCH_4 of 1.77 µatm.

1.4.3 Determination of CO_2 fluxes and kCO_2

Instantaneous CO_2 fluxes (f_{CO2}) (mmol m^{-2} d^{-1}) across the water-air interface were measured in situ using floating chambers, following Vachon *et al.* (2010). The circular plastic chamber, with a surface area of 0.09 m^2 and volume of 16 L, was covered with aluminum foil to reduce solar heating and equipped with an internal thermometer to monitor temperature changes that may affect the exchange rates during the measurements. The floating chamber was connected to an infrared gas analyzer (PP-system, model EGM-4) via enclosed re-circulating system providing a continuous reading of the CO_2 concentrations in the chamber. The chamber was placed on the

water surface, pressure was released, and the pCO_2 in the chamber was subsequently recorded every minute, for 10 minutes. The rates of change in pCO_2 in the chamber were used to estimate f_{CO2} (mol m^{-2} d^{-1}), with the following equation:

$$f_{CO_2} = \left(\frac{s * V}{V_m * S} \right) * f \qquad (1.2)$$

where (*s*) is the rate of change of the gas in the chamber (µatm min^{-1}), (V) is the volume of the chamber in liters (L), S is the surface area of the chamber (m^2), (V_m) (molar volume) is the molar volume of one mole of gas (L mol^{-1}), and (*f*) is a conversion factor from minutes to day (1d = 1440 min).

f_{CO2} was further used to estimate k_{CO2} by inverting the equation describing Fick's law as follows:

$$k_{CO_2} = \frac{f_{CO_2}}{kH(pCO_{2water} - pCO_{2air})} \qquad (1.3)$$

where k_{CO2} is the gas transfer velocity in m d^{-1} specific for CO_2; f_{CO2} is the measured CO_2 flux between the surface water and the atmosphere in the floating chamber, kH is Henry's constant adjusted for salinity and temperature, and ΔpCO_2 is the difference between CO_2 partial pressure in the surface waters and the atmosphere (µatm). To simplify the exploration of regional patterns of gas exchange across the fluvial network, we standardized k_{CO2} to a Schmidt number of 600 to derive a k_{600}, with following the equation from Jähne et al. (1987)

$$k_{600} = \frac{k_{CO_2}}{\left(Sc_{CO_2}/600\right)^{-n}} \quad (1.4)$$

where Sc_{CO2} is the CO_2 Schmidt number at the stream water temperature (Wanninkhof, 1992), and n was fixed at 2/3, which corresponds to surface roughness resulted at wind speed of <3.7m s^{-1} accordingly to (Guérin *et al.*, 2007).

1.4.4 Quantifying diffusive and none-diffusive CH_4 fluxes

Similarly to the f_{CO2}, the CH_4 fluxes (f_{CH4}) were measured with the floating chamber, at the same time the CO_2 flux was determined, except that the change in pCH_4 in the floating chamber was determined by sampling the chamber air at 0, 5 and 10 minutes, by withdrawing 30 ml from chamber's headspace through an enclosed system of syringes. These air samples were stored in airtight vials and analyzed in the laboratory as described above. The rate of change of pCH_4 in the floating chamber was used to calculate the f_{CH4} with the equation 2 as shown above for CO_2.

Due to the low solubility of CH_4 in freshwater, f_{CH4} to the atmosphere not only occur via diffusion but also through none-diffusive pathways, such as ebullition, which may contribute significantly to the total fluvial CH_4 emissions (Bastviken *et al.*, 2004, Baulch *et al.*, 2011). In this regard, the k_{CH4} derived from the f_{CH4} measured in the floating chambers may reflect both diffusive fluxes as well as potentially non-diffusive f_{CH4}, and for this reason the resulting empirical k_{CH4} are often much higher than those predicted by Fick's law relative to k_{600} (Prairie & del Giorgio, 2013). In order to quantify the contribution of non-diffusive f_{CH4} to the overall f_{CH4}, we first calculated

the theoretical diffusive k_{CH4} on the basis of our empirically-determined k_{600}, using the following equation 5 adjusted for CH_4

$$k_{CH_4} = \frac{k_{600}}{(600/Sc_{CH_4})^{-n}} \quad (1.5)$$

This yields an estimate for a strictly diffusive k_{CH4}, which we used to back-calculate a theoretical diffusive CH_4 flux (mmol m^{-2} d^{-1}) with the following equation;

$$fD_{CH4} = k_{CH4} * kH\ (pCH_{4water} - pCH_{4air}) \quad (1.6)$$

where fD_{CH4} is the diffusive flux of CH_4 at the interface water-air according to Fick's law; k_{CH4} is the gas transfer velocity of CH_4 derived from the k_{600}; kH is the Henry's coefficient (adjusted for ambient salinity and temperature); and the pCH_{4water} and the pCH_{4air} are the partial pressure of CH_4 in water and air (1.77 µatm), respectively. We then used the difference between fD_{CH4} and the f_{CH4} measured from the floating chambers as an estimate of the potential non-diffusive f_{CH4} (Prairie & del Giorgio, 2013).

1.4.5 Rivers and streams characterization and regional-scale patterns

To describe the regional patterns of fluvial CO_2 and CH_4 emissions, we linked the above-described variables (pCO_2, pCH_4, k_{600}) to basic river and stream properties that integrate the positioning in the landscape and morphometric characteristics of

streams and rivers within the fluvial network. A number of stream properties were determined, either on site or from digitized maps available at Natural Resources Canada (National Topographic DataBase (NTDB) under a resolution of 1:50 000 scale. All geographical analyses were performed on ArcMap GIS 9.3 with hydrological extensions. For each of the sampled sites, we delineated the catchment area and calculated the cumulative length of digitized stream and river segments within this area. This corresponded to the total length of streams and rivers upstream of the sampled site (Total Stream Length, TSL), which was used as an index of the position of each river within the fluvial network hierarchy. This index was analog to the Strahler stream order but allowed to better explore gas dynamics on continuous gradients.

Once the patterns were established, we manually determined the Strahler stream order (Strahler, 1957) from the digitized streams and rivers for each of the 46 sampled sites in order to further facilitate the landscape level estimation of gas emissions. Sites that were too narrow to appear in the digitized maps were considered as a separate category, stream order 0. The channel morphometry, width and depth, at the cross section of the sampling location was measured using a measuring tape or a solar depth meter. The available material did not allow measuring these morphological properties directly on site for the largest rivers (stream order 6), and we used satellite images to estimate the average width in the latter.

1.4.6 Determining total river and stream areal coverage

Streams and rivers are represented on digitized maps as fragmented segments, which prevent any large-scale estimations of the abundance or surface occupied by streams and rivers on a continuous basis according to their sizes or lengths. Consequently, we chose to base our regional scale estimate of fluvial area on the tributary classification systems of Strahler stream orders, which is correspondent to the total stream length, and calculated the total area covered by each of the 6 different stream orders present in the fluvial network of both regions. We performed a digital elevation model (DEM) interpolation to calculate the length (m) of each stream orders in the two regions, which used the digitized topography to generate a segment raster map representing a classified linear coverage of stream and rivers according to their Strahler stream orders. This interpolation slightly overestimated the total cumulative length of streams and rivers (from order 1-6) in comparison to available digitized streams and rivers. We assumed that this discrepancy represented the smallest headwater streams, narrower than 0.5 m, included in our survey that did not figure on digitized maps. We finally combined the estimated stream length (m) per stream order with the average channel width (m) corresponding to each stream order from the data collected on the field for our 46 sampled sites. This yields us an estimate of the total area (m^2) occupied by each stream order in the fluvial network of both regions.

1.4.7 Quantifying CO_2 and CH_4 emissions during the spring thaw

We have in addition, carried out measurements of pCO_2 and pCH_4 and of gas fluxes both under the ice and right after ice melt in a subset of the rivers; we have used the resulting patterns in gas build-up to incorporate late winter and early spring gas fluxes to our open-water estimates of regional CO_2 and CH_4 emissions, in order to derive annual regional emissions that account for this critical period of the year. We quantified the CO_2 and CH_4 emissions during the spring thaw using the average CO_2 and CH_4 fluxes to the atmosphere measured with floating chambers in mid-April, approximately 7 days after the start of the ice-break, and in early-May, approximately 21 days after the start of the ice-break. We assumed a linear relationship in the average CO_2 and CH_4 fluxes between mid-April to early-May, and used this relationship to estimate the average daily CO_2 and CH_4 fluxes for the entire spring thaw period (approximately 30 days).

1.4.8 Regional estimates of fluvial CO_2 and CH_4 emission

We combined the patterns in pCO_2, pCH_4 and gas exchange (k_{600}) to estimates the diffusive CO_2 and CH_4 fluxes in relation to the Strahler stream order (equation 1), and up-scale these fluxes for the entire fluvial network in a region covering 44 182 km^2. This approach was developed to promote a better understanding of the underlying processes controlling the fluvial C-gases emissions across large spatial gradients. The CO_2 and CH_4 diffusive emissions were calculated by combining our

estimates of areal extend (km^2) of each stream order to their respective mean surface water pCO_2 and pCH_4 (µatm) and k_{600} (m d^{-1}). The average non-diffusive CH_4 emissions per stream order were added to the diffusive fluxes to yield an estimate of total CH_4 emissions.

To develop a more comprehensive estimate, the CO_2 and CH_4 emissions from the stream order 0 category were calculated separately but were ultimately added to the emissions for the stream order 1 category. The total annual emissions were determined by combining the estimated CO_2 and CH_4 emissions for the spring thaw period (30 days) to the estimate for the ice-free season (184 days), representing a combined 214 days. This time allowance was made in agreement with continuous water level and temperature records from level loggers (Trutrack, WT-HR Mark 3 data-loggers, Intech intruments LTD) deployed on a subset of 13 streams. The resulting data allowed us to reconstruct the annual temperature and discharge cycle for streams of different order. The ice-covered period (151-day from November to April) was considered neutral in terms of gas fluxes. This assumption is likely an unrealistic and may result in an overall underestimation of the annual fluxes and needs to be further investigated.

1.4.9 Statistical analysis

Statistical analyses were executed on JMP©9.3 (SAS institute). Data were log transformed in order to meet conditions of homoscedasticity and normality when needed. We performed simple linear regression (SLR) and covariance analyses

(ANCOVA) to test significant differences in the patterns observed with the SLR modeled between either the two regions (Abitibi and James Bay) or between the different sampling periods of the ice-free season. In several cases, data points were removed from the analysis in order to meet the statistical assumptions, in which cases we analyzed the Cook's distances to validate the removal of those data points. Those data points are presented and identified on the figures, and were also integrated in the up-scaling exercises to derive regional fluvial emissions.

1.5 Results

1.5.1 Regional pattern of surface water pCO_2 and pCH_4

Despite contrasting landscape properties between the Abitibi and James Bay regions (Table 1.1), the average pCO_2, pCH_4, k_{600}, fCO_2 and fCH_4 were not significantly different between the two regions (Table 1.2). The surface water pCO_2 and pCH_4 was highly supersaturated relative to the atmosphere in the fluvial network of both regions, ranging 2 orders of magnitude for pCO_2 and over 4 orders of magnitude for pCH_4 (Table 1.2)

Table 1.2: Summary table showing averages and ranges of surface water pCO_2, pCH_4 gas exchange velocity (k_{600}) derived from chamber measurement and fCO_2 and fCH_4 obtained directly from chamber measurements. Averages for the two regions, Abitibi and James Bay are also presented with the respective p-value for statistical differences between regions.

	All Sites			Abitibi	James Bay	t-test
	average	min	max	average	average	p-value
n		134		104	30	
pCO_2 (µatm)	2 959	509	10 537	3 125	2 384	0.07
pCH_4 (µatm)	1 781	24	28 683	2 030	922	0.16
k_{600} ($m\ d^{-1}$)	1.34	0.10	11.59	1.41	1.14	0.49
fCO_2 ($mg\ C\ m^{-2}\ d^{-1}$)	888	40	5 879	905	875	0.89
fCH_4 ($mg\ C\ m^{-2}\ d^{-1}$)	97	0.33	2 576	122	37	0.27

We observed a power-law decrease of both mean open water surface water pCO_2 and pCH_4 (µatm) with increasing total stream length (TSL) (m) (Figure 1.2a and b).

$Log\ pCO_2 = 3.61 - (0.18 * \text{Log TSL})$	$r^2=0.68$ n=41	p<0.0001	(1.7)
$Log\ pCH_4 = 3.45 - (0.34 * \text{Log TSL})$	$r^2=0.69$ n=39	p<0.0001	(1.8)

Their was no statistically significant difference between large-scale patterns for neither pCO_2 nor pCH_4 between the Abitibi and James Bay regions (ANCOVA (Figure 1.2a) intercept ($p > 0.43$) and slope ($p > 0.61$); ANCOVA (Figure 1.2b) intercept ($p > 0.17$) and slope ($p > 0.76$)).

The k_{600}, derived from floating chamber measurements, was not significantly different between the two regions (Table 1.2) but varied significantly throughout the seasons ($p<0.0001$), following changes in discharge and water velocity. Autumn (October) and spring (late-April & early-May) high-flow periods, had the highest average k_{600} with 1.65 (m d^{-1}) and 2.60 (m d^{-1}) respectively, whereas the lowest average k_{600} (0.68 m d^{-1}) occurred during summer base-flow (June to August). There was a significant positive relationship between the k_{600} and the TSL (Figure 1.2c):

$Logk_{600} = -0.42 + (0.18 * \text{Log TSL})$	$r^2=0.28$	n=44	p<0.0001	(1.9)

As opposed to gas concentration (pCO_2 and pCH_4) and k_{600}, there was no significant pattern of either fCO_2 or fCH_4 with TSL, resulting in a rather constant average rate across the fluvial network.

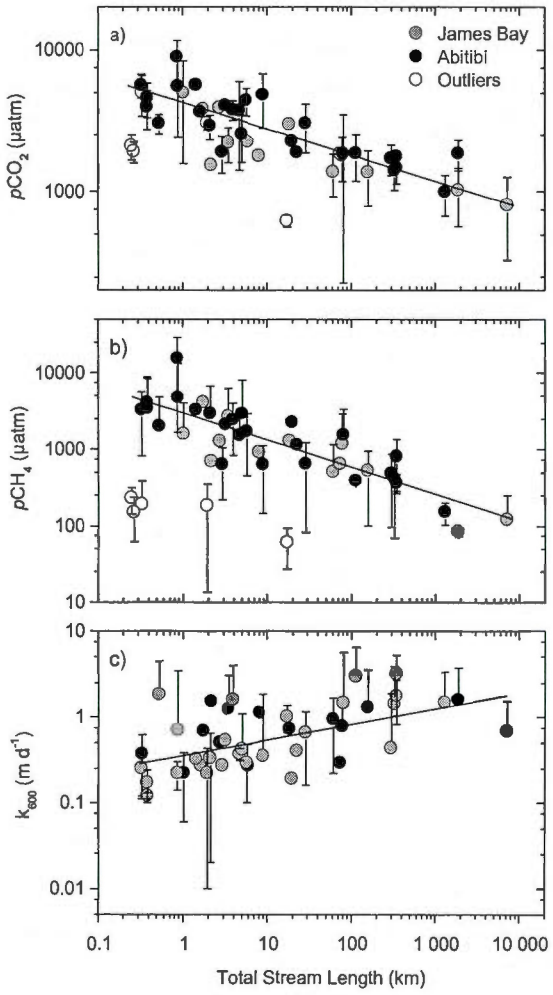

Figure 1.2 : a) Surface water pCO_2 (upper), b) pCH_4 (lower) (µatm) and c) gas exchange coefficient (k_{600}) as a function of the total stream length above the sampling site (TSL) (km) on logarithmic scales (Equation 1.7,1.8 and 1.9). Each circle represents the average pCO_2, pCH_4 or k_{600} for each of the 46 different streams and rivers sampled over the ice-free season (from May to October). Error bars represent the variability between the sampling periods. The dark gray and light gray circles

represent the sites in the Abitibi and James Bay region respectively, while the open circles represent the sites that were removed from the analysis (Equation 8, 9 and 10). Three small headwater streams, for which the pCH_4 was distinctively below the regional trend throughout the open-water season, were excluded from the analysis. The pCH_4 was especially variable among the smallest headwater streams (stream order 0) within both regions, ranging from 59 to 9 611 µatm. We speculate that this large range in CH_4 concentration reflects the variability in CH_4 inputs from the catchment to the headwater streams (Hope *et al.*, 2004). Two streams sampled in isolated hill-slopes, where the stream flow was rapid, had a pCO_2 and pCH_4 well below the regional trend and were also excluded from the analysis. We speculate that this was possibly due to turbulence-enhanced atmospheric evasion (Macintyre *et al.*, 1995, Wallin *et al.*, 2011), maintaining surface water C-gas concentration low throughout the open water season.

1.5.2 Regional estimates of fluvial CO_2 and CH_4 emissions

The fluvial network in both regions covered a total of 191 km^2, approximately 0.5% of the total landscape area (44 182 km^2). The drainage density of the Abitibi and James Bay region was in average 1.07 km^{-1}, which is characteristic of permeable landscape with reduced potential for runoff. The areal coverage of each Strahler stream orders [1 to 6] was roughly evenly distributed across both regions, averaging 31.8 km^2. The largest surface, however, was covered by stream order 1 (38.7 km^2), which occupied about 20% of the fluvial networks total area (Table 1.3). The smallest headwater streams (stream order 0) was combined with the stream order 1, but accounted for only 29% of the surface of stream order 1, and 6% of the total fluvial network.

Table 1.3: Characteristics of the fluvial network areal distribution for each Strahler stream order estimated with the DEM interpolation.

Order	n	Average TSL (km)		Average channel width (m)	Cumulative stream segment length in the region (km)	Total surface in the region (km^2)
0	5	0.33	(±0.06)	0.8	13 718	10.97
1	14	1.74	(±1.01)	1.85	15 018	27.78
2	9	7.06	(±4.66)	2.39	11 412	27.27
3	6	39.44	(±22.8)	7.22	4 323	31.21
4	7	156.85	(±123)	18.35	1 643	30.14
5	2	337.73	(±13.9)	41.79	827	34.58
6	3	3466.11	(±3 256)	120	242	28.99

The results and data used to produce the regional scale estimates (Table 1.4) suggest that the contribution to total fluvial C emission decreased with increasing stream order, from the highest contribution from the order 1 streams (8,136 tons of CO_2-C and 1,208 tons of CH_4-C) to the smallest from the order 6 streams (2,394 tons of CO_2-C and 29 tons of CH_4-C). The emissions from the stream order 1 category include also the emissions from the small headwater streams (stream order 0), which represented 842 tons of CO_2-C and 60 tons of CH_4-C. The fluvial network released a total of 30,557 tons of CO_2-C and 2,543 tons of CH_4-C to the atmosphere over ice-free period (184 days). Considering that one gram of CH_4 as a the global warming potential of 23 grams of CO_2 (Solomon *et al.*, 2007) our estimates show that the fluvial network emitted to the atmosphere a total of 51 915 tons of GHG (in CO_2 equivalent) during the ice-free season, with 41% contributed by CH_4.

Table 1.4: Synthesis table of the regional scale extrapolation of the fluvial network CO_2 and CH_4 fluxes in the region of Abitibi and James Bay (covering a total area of 44 182 km^2) for the ice-free season, corresponding to 184 days (from May to October inclusively). The estimations of fluvial greenhouse gas (GHG) emission consider that CH_4 has global warming potential 8.4 times stronger than CO_2 in terms of C-mass. Additional rows at the bottom of the table present the estimates for the emissions during the spring thaw period, and ebullitive CH_4 emissions, and finally the total annual emissions.

Strahler Stream Order	*n*	pCO_2	pCH_4	k_{600}	fCO_2	Diffusive fCH_4	Non-Diffusive fCH_4	CO_2 emission	CH_4 emission	GHG emission
		µatm	µatm	m d^{-1}	mg C m^{-2} d^{-1}	mg C m^{-2} d^{-1}	mg C m^{-2} d^{-1}	Tons of C	Tons of C	Tons of C (eq.CO_2)
1	19	3 980	3 183	0.56	1 141	42.53	126.82	8 136	1 208	18 280
2	9	3 184	1 736	0.58	998	23.01	43.42	5 006	333	7 807
3	6	2 209	1 005	0.49	462	10.48	12.84	2 652	134	3 778
4	7	1 569	647	1.38	992	22.48	19.78	5 500	234	7 469
5	2	1 443	585	2.28	1 079	31.84	63.16	6 867	604	11 944
6	3	937	146	1.24	449	4.35	1.07	2 394	29	2 637
Total emission during the ice free season (184 d)								30 557	2 543	51 915
Total emission during the spring thaw (30 d)								12 779	74	13 401
Total annual fluvial emission (214 d)								43 336	2 617	65 316

1.5.3 Diffusive and non-diffusive CH_4 fluxes

To quantify the non-diffusive component of the total fCH_4, we compared the fCH_4 measured in the floating chambers with the diffusive fCH_4 (fD-CH_4) calculated based on the empirically-determined k_{600}. The comparison between the fCH_4 and the fD-CH_4 (Figure 1.3a), with most of the values falling above the 1:1 line, indicates the presence of none-diffusive CH_4 fluxes, averaging 72.9 mg C $m^{-2}d^{-1}$ and ranging from zero to 2 421 mg C m^{-2} d^{-1}. There was a positve relationship between these estimated non-diffusive fCH_4 (mmol m^{-2} d^{-1}) and the CH_4 supersaturation (pCH_4:1.77) ($SRCH_4$) (Figure 1.3b):

$$\text{Log N-D } fCH_4 = -2.81 + 1.03 * \text{Log } SRCH_4 \qquad r^2=0.43 \quad n=55 \; p<0.0001 \qquad (1.10)$$

The non-diffusive CH_4 fluxes contributed significantly to the total CH_4 fluxes, generating approximately 1 713 tons of CH_4-C or 67% of total CH_4 emissions. This high contribution was proportional to the very elevated CH_4 saturation observed in the fluvial networks (Figure 1.3b)

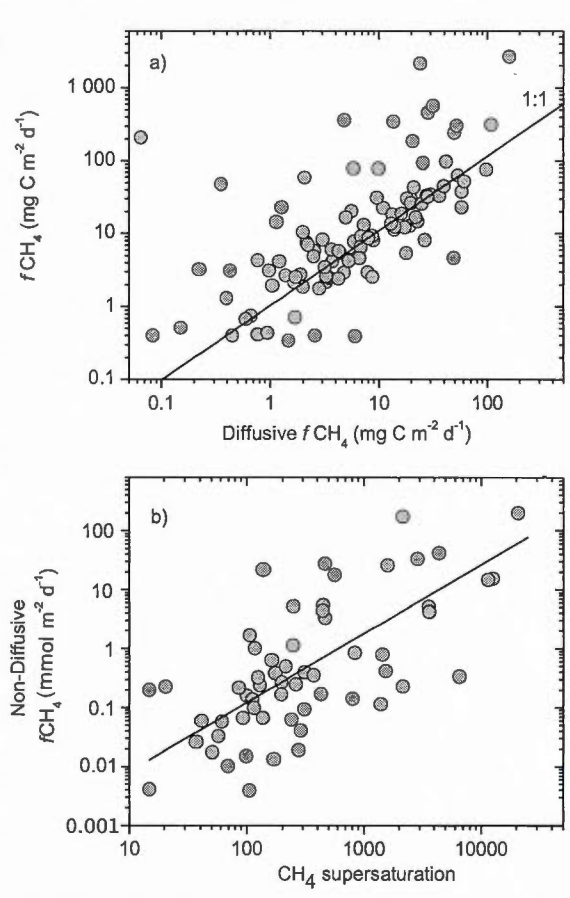

Figure 1.3 : a) total fCH_4 (mg C m^{-2} d^{-1}) measured with the floating chamber as a function of the strictly diffusive fCH_4 (mg C m^{-2} d^{-1}) derived from the k_{600}. The 1:1 line demonstrates the equivalence of both fluxes and shows that non-diffusive fCH_4 occur very frequently (circles falling above the 1:1 line) and that total fCH_4 can reach two to three orders of magnitude above strictly diffusive fCH_4. b) Non-diffusive fCH_4 (mg C m^{-2} d^{-1}) as a function of surface water pCH_4 (µatm), following a positive power law relationship. Data was displayed on logarithmic scales for both axes and figures (Equation 1.10).

1.5.4 CO_2 and CH_4 dynamics during spring thaw

There was evidence of gas accumulation during winter, with pCO_2 and pCH_4 peaking under the ice-cover at the end of the winter, averaging 9 165 µatm pCO_2 n=13 (range 2 365 to 33 853 µatm), and 14 863 µatm pCH_4 n=13 (range 103 µatm to 162 933 µatm, respectively (Figure 1.4 a and b). Following ice-break, both pCO_2 and pCH_4 decreased rapidly and gradually, returning to ice-free season averages (Figure 1.4 a and b). During the spring thaw, the fCO_2 were twice as high as the average fluxes measured during the ice-free season, averaging 2 766 mg C m^{-2} d^{-1} in April and 1 529 mg C m^{-2} d^{-1} in May (Figure 1.4 c). In contrast, the fCH_4 were lower in April and May than during the ice-free season, averaging 16.9 mg C m^{-2} d^{-1} and 5.8 mg C m^{-2} d^{-1}, respectively (Figure 1.4 d). These fluxes, integrated over a period of 30 days, resulted in an evasion from the entire fluvial network of 12 779 tons of CO_2-C and 74 tons of CH_4-C to the atmosphere. Added to the ice-free seasons emissions, the fluvial network released a total of 43 336 tons of CO_2-C and 2 617 tons of CH_4-C during the 214 days open water period (Table 1.4), indicating that spring thaw GHG emissions contributed 29% to the annual CO_2 emission and 3% of the annual CH_4 emission.

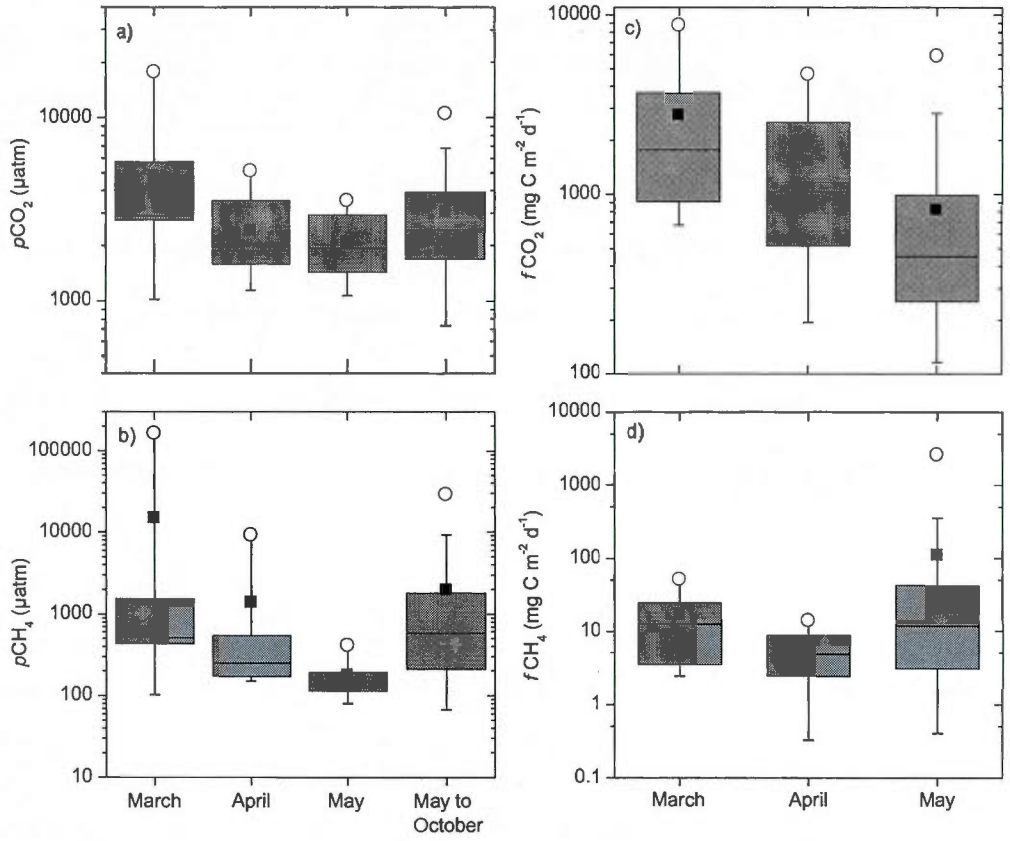

Figure 1.4 : Box-plot showing the distribution of surface water pCO_2 (a) and pCH_4 (b) for the different sampling periods; in March at the end of the ice-covered period, in mid-April approximately 1 week following the ice break, in early-May approximately 3 weeks following the ice break and for the overall ice-free season, from late May to the end of October. Box-plot showing the distribution of fCO_2 (c) and fCH_4 (d) from chamber measurements during different sampling periods; in mid-April approximately 1 week after the ice break, in early-spring. Black squares and white circles represent the average value and the maximal value respectively.

1.6 Discussion

1.6.1 Regional patterns of pCO_2 and pCH_4

The surface water pCO_2 in the fluvial network of Abitibi and James Bay was in the upper range of published values from other boreal regions (Humborg *et al.*, 2010, Koprivnjak *et al.*, 2010, Teodoru *et al.*, 2009, Wallin *et al.*, 2010). Similarly, the surface water pCH_4 corresponded to the upper range of values reported in arctic and temperate rivers (Deangelis & Lilley, 1987, Kling *et al.*, 1992) and streams (Baulch *et al.*, 2011, Billett & Moore, 2008, Hope *et al.*, 2004, Jones & Mulholland, 1998b). The scarcity of published data in boreal streams and rivers does not allow us to compare our results with others studies from the same biome.

Overall, it appears that the low topography, and presumably the extended water residence time it generates in the region may play a key role in controlling C-gas concentrations. In fact, the low topography was one of the rare common feature present in both regions, where CO_2 and CH_4 concentrations displayed similar patterns in the fluvial network (Table 1.2 and Figure 1.2), and such, in spite of many important differences e.g abundance of wetlands and peatlands, degree of beaver impoundments on streams, forest and soil coverage (Table 1.1). The low relief of Abitibi and James Bay presumably slows down the overland and stream runoff (McGuire *et al.*, 2005, Tetzlaff *et al.*, 2011), and may foster high river pCO_2 and pCH_4 by extending the microbial contact time with organic substrates in soils, streams, and hyporheic zone

(Battin *et al.*, 2008, Hlavacova *et al.*, 2006, Mulholland, 1981). The flat topography may also promote CH_4 production by decreasing drainage quality and generating permanently water-saturated patches in soils and streambeds where oxygen is poorly available (Arnold *et al.*, 2005, Dahm *et al.*, 1991, Ullah & Moore, 2011).

The surface water pCO_2 and pCH_4 decreased as a power function of the TSL, in both Abitibi and James Bay (Figure 1.2 a and b). This pattern of declining pCO_2 with increasing stream order has been reported for other regions (Butman & Raymond, 2011, Crawford *et al.*, 2013, Humborg *et al.*, 2010, Striegl *et al.*, 2012, Teodoru *et al.*, 2009, Wallin *et al.*, 2010), and is typically explained by the dilution of the lateral soil-water inputs (Crawford *et al.*, 2013, Wallin *et al.*, 2010), atmospheric gas loss (Dawson *et al.*, 1995, Oquist *et al.*, 2009), or decreasing organic C degradation with increasing stream order (Battin *et al.*, 2008, Dawson *et al.*, 2001, Finlay, 2003). In contrast to pCO_2, there have been few descriptions of patterns in pCH_4 within river networks. Jones and Mulholland (1998a) found that pCH_4 increased slightly downstream in a highland river continuum, a pattern that is opposite to ours (Figure 1.2 b), while Striegl *et al.,* (2012) and Carwford et al., (2013) reported a similar pattern to ours in the Yukon river system which is a rather flat region as well. In typical highland regions, stream turbulence tends to decline downstream with increasing discharge, creating more favorable conditions for in situ CH_4 production in larger rivers (Jones & Mulholland, 1998b). Our results thus suggest that the regional patterns of pCH_4 are similar to those of pCO_2 in these lowland boreal networks, in respond to the landscape attributes and hydrological regimes. In addition, these

patterns emerge even when combining systems from distinct catchments and suggest that the decline of pCO_2 and pCH_4 with increasing stream size may be independent of specific catchment properties. Although these patterns provide little insight on the origins or underlying processes driving the recurrent decrease of pCO_2 and pCH_4 with increasing stream size, they highlight that C-gas concentration can be predicted on the basis of simple geographical indexes. Since TSL generally correlates well with catchment area, drainage density or stream discharge, it opens opportunity for a broad exploration of C-gas patterns and quantification of C-gas fluxes.

1.6.2 Patterns of k_{600} and the influence of hydrology

In flowing waters, the k_{600} is mainly governed by the internal turbulent energy (Macintyre *et al.*, 1995, Wallin *et al.*, 2011), such that gas exchange rates tend to be linked to stream flow, itself related to stream morphology and slope (Melching & Flores, 1999, Wallin *et al.*, 2011, Wanninkhof *et al.*, 1990). In these flat landscapes, water velocity increases with stream size and order, which presumably generates the increase of the k_{600} with TSL (Figure 1.2c). This pattern differs from previous studies carried out in landscapes with more pronounced relief, which instead report a systematic decrease of the k_{600} along fluvial networks, with values ranging from 3-12 m d^{-1} in headwater streams (Genereux & Hemond, 1992, Wallin *et al.*, 2011) to 1-2 m d^{-1} in rivers (Cole & Caraco, 2001, Raymond & Cole, 2001, Striegl *et al.*, 2012).

Our results thus suggest a second alternative pattern of the k_{600} along fluvial networks specific to regions of flat relief. The first pattern, which describes the k_{600} decreasing with stream order, can usually be found in regions of higher elevation, whereas in lowland regions, k_{600} here tend to increases with stream order (Sand-Jensen & Staehr, 2011). In both cases, k_{600} converges to values around 1-2 m d^{-1} for large rivers (stream order 6 and beyond) (Raymond & Cole, 2001), but the largest discrepancies occurred at the lowest stream orders. According to this discrepancy, neither the pattern in k_{600} reported for other regions, nor the average values, can be extrapolated to river networks in lowland boreal regions.

In this study, the k_{600} was determined from floating chamber measurements, whereas some of the studies cited above used gas tracers to quantify rates of re-aeration. We acknowledged that the floating chamber approach can be problematic for fast flowing waters, but the vast majority of rivers in our study region had extremely low water velocities which were well-suited for the use of this method. However it is still possible that under these circumstances, the chamber method may have likely induced an overestimation of the actual flux and its related k_{600}, which tend to occur under low turbulent condition (Vachon *et al.*, 2010). Contrarily, our measured k_{600} were found to be lower than expected, the opposite of what we could apprehend from chamber measurements influence. In addition, available empirical models, developed by (Raymond *et al.*, 2012), have yield similar ranges of k_{600} values as the ones obtained from our chamber measurements, and also similar patterns to the ones

observed in figure 1.2c. In this case, we thus assumed that the chamber-induced bias was limited and the k_{600} measurements discrepancies are a true landscape effect.

1.6.3 Regional scale estimates of fluvial CO_2 and CH_4 emissions

Our regional estimates of CO_2 and CH_4 emissions emphasize the large contribution of small order streams (Table 4). Although similar patterns have been observed before (Crawford *et al.*, 2013, Koprivnjak *et al.*, 2010, Teodoru *et al.*, 2009), in the case of the Abitibi and James Bay region, these high emissions were largely driven by the very high CO_2 and CH_4 concentrations, whereas in previous studies the high turbulence and the resulting rapid gas loss to the atmosphere from low order streams was the main driver of these emissions. The contribution to total fluvial CO_2 and CH_4 emissions decreased with stream orders, following the pattern of pCO_2 and pCH_4 (Table 4). This suggests that in lowland regions, where the k_{600} remains overall low (Figure 1.2c), the variability in fluxes is mainly driven by either the delivery of terrestrially produced CO_2 and CH_4 or in-stream production rather than by turbulence and gas exchange. The contribution of stream order 6 was especially low in result to a particularly low average k_{600} (Table 4). This low estimate could possibly result from the fluxes measurements being undertaken from shore and thus may slightly underestimate the actual fluxes and contribution for the largest rivers in the region.

Expressed per unit landscape area, the fluvial network in the Abitibi and James Bay regions released a total of 1.48 tons of C (CO_2-equivalent) km^{-2} yr^{-1} to the atmosphere. This compares well with previous estimates developed by other studies, where the boreal fluvial network released 2.15 tons of CO_2-C km^{-2} yr^{-1} (Teodoru *et al.*, 2009) in the Eastmain region of northern Québec, 1.84 tons of CO_2-C km^{-2} yr^{-1} (Humborg *et al.*, 2010) and 1.56 tons of CO_2-C km^{-2} yr^{-1} (Jonsson *et al.*, 2007) in Sweden, but is largely bellow the estimates from the Yukon river basin with 2.6 and 9.5 tons of C (CO_2 eq) km^{-2} yr^{-1} (Crawford *et al.*, 2013, Striegl *et al.*, 2012). Our results, however, emphasize the major role of the fluvial network in total emissions, which up to now has not been included in regional aquatic carbon budgets (Battin *et al.*, 2009). Expressed as CO_2 equivalents, CH_4 accounted for a major part (34%) of the annual fluvial GHG warming potential, especially in the smaller streams where is accounted for up to 55% (Table 4). This surprisingly large contribution of CH_4 implies that current budgets, based solely on CO_2, likely underestimate the role of fluvial networks as GHG emitters by almost half.

1.6.4 Contribution of fluvial CH_4 emissions and the non-diffusive fCH_4

We have demonstrated that non-diffusive fCH_4 may be a significant process in these fluvial networks, as it occurs frequently and sometimes reaches one order of magnitude above the strictly diffusive fCH_4 (Figure 1.3a). Discrepancies between total fCH_4 (measured in floating chamber) and strictly diffusive fCH_4 (estimated on

the basis of k_{CO2}) have been reported previously in lakes and reservoirs (Prairie & del Giorgio, 2013) and rivers (Beaulieu *et al.*, 2012) and can be inferred in (Billett & Harvey, 2012, Striegl *et al.*, 2012). These discrepancies are presumably due to the low solubility of CH_4 and its tendency to concentrate into microscopic bubbles, especially under very high CH_4 saturation. These bubbles may then escape to the atmosphere and cannot be incorporated in estimates based on k_{CO2}. We observed that the apparent non-diffusive fCH_4 also increased as a power function of the surface water pCH_4 (Figure 1.3b), in accordance with the above mechanism. Note that the relationship illustrated on figure 1.3 (equation 1.10) is almost identical to the one reported in Prairie & del Giorgio (submitted), suggesting that this mechanism may be widespread across the aquatic realm. The non-diffusive f_{CH4} contributed to an extremely large fraction of the of the CH_4 emission (on average 56%) during the ice-free season in the fluvial network of Abitibi and James Bay (Table 1.4), underscoring the importance of incorporating this pathway in estimating the total CH_4 emissions.

Our estimates of fluvial CH_4 emissions likely do not include macro-bubble mediated (ebullition) fluxes, which involves the localized release of large CH_4 rich-bubbles originating from the sediments (Bastviken *et al.*, 2004), which were presumably not captured by our floating chambers given that they were only set for 10 minutes periods and covered a relatively small area of the stream surface. Previous studies of similar rivers in a neighboring region of Canada concluded that this ebullitive fCH_4 contributed between 20-67% to the measured total stream CH_4 fluxes (Baulch *et al.*, 2011). Indicating that our estimations of total CH_4 emissions, which

are already surprisingly large, possibly still underestimate the total CH_4 fluxes from these boreal fluvial networks.

1.6.5 Importance of CO_2 and CH_4 emissions during spring thaw

Winter accumulation of biogenic gases has been documented in a large number of boreal lakes (Demarty *et al.*, 2011, Dillon & Molot, 1997, Karlsson *et al.*, 2008, Kortelainen *et al.*, 2006, Semiletov, 1999) and was found to generate important gas fluxes during the short period of the spring thaw, contributing up to 52 % of the open water emissions (Algesten *et al.*, 2004, Demarty *et al.*, 2011, Huotari *et al.*, 2009, Michmerhuizen *et al.*, 1996), but similar estimates are lacking for boreal flowing waters. We found that the winter pCO_2 was significantly higher than during the ice-free season ($p>0.0003$) (Figure 1.6a), whereas winter pCH_4, although high, remained in the range of saturation measured during the ice-free season (Figure 1.6b). There was a progressive decline in pCO_2 and pCH_4 during the 1-month spring thaw, which coincided with high measured fCO_2 (although not fCH_4) during the period (April and May) (Figure 1.6 c and d). The fluvial CO_2 and CH_4 emissions during the 30-day period of the spring thaw contributed on average 29% of the annual fluvial CO_2 emission (12 779 tons of C) and 3% to CH_4 emission (74 tons of C).

These disproportionately large CO_2 emissions during the spring thaw suggest a constant replenishment of surface water pCO_2 throughout the month by terrestrial inputs of organic and inorganic material, possibly supporting these high fluxes (Agren *et al.*, 2010, Agren *et al.*, 2007, Laudon *et al.*, 2004). On the other hand, CH_4 emission

barely peaked in the spring, suggesting modest replenishment during the spring thaw, as CH_4 production in stream appears strongly modulated by water temperature (Billett & Moore, 2008, Moore & Dalva, 1993, Ullah & Moore, 2011). Nonetheless, spring thaw CO_2 and CH_4 emissions represented 21% of the annual GHG emissions, in the same range of values found in boreal lakes (Algesten *et al.*, 2004, Demarty *et al.*, 2011, Huotari *et al.*, 2009) and indicates that capturing this brief period is essential for building accurate annual budgets for boreal rivers and streams, and not only for boreal lakes.

1.6.6 Relative significance of fluvial CO_2 and CH_4 emissions

Boreal rivers and streams were found to contribute a disproportionate fraction (up to 65%) of total aquatic CO_2 emissions in relation to the surface they occupy (Aufdenkampe *et al.*, 2011, Humborg *et al.*, 2010, Jonsson *et al.*, 2007, Teodoru *et al.*, 2009). For Methane however, it has often been assumed that fluvial networks contribute modestly (in the order of 4%) to total aquatic CH_4 emissions (Bastviken *et al.*, 2011). By comparing the estimated CO_2 and CH_4 emissions from the fluvial network in Abitibi and James Bay to previously documented averages CO_2 and CH_4 fluxes from boreal lakes, we can further asses the potential contribution of these emission in a regional aquatic GHG budget (Table 1.5). Applying these upper and lower ranges of lake CO_2 and CH_4 fluxes (Table 1.5), to the total number and total areal coverage of lakes in the region (3 825 km^2), we estimated that the total aquatic

emissions in the Abitibi and James Bay regions, including lakes and rivers, would range from 207 to 544 Gg of C as CO_2, and 4.6 to 7.7 Gg of C as CH_4, annually (over a 214 days open-water period) (Table 1.5). The fluvial network would thus contribute between 8 to 21% of the total aquatic CO_2 emissions, but up to 35 to 59 % of the total aquatic CH_4 emissions, while covering only 4.3% of the total aquatic surface. This type of exercises have rarely been performed for boreal aquatic CH_4 emissions and in this case, challenge our current perception of flowing waters as negligible sources of atmospheric CH_4.

Table 1.5: Regional scale budgets of total aquatic CO_2 and CH_4 emission for the Abitibi and James Bay regions. Lake CO_2 and CH_4 emissions were estimated from published values combined with the areal coverage for lakes and reservoirs in the studied regions, determined from NTDB 1:50 000 and corresponding to of 3 825 km^2. Rivers and stream CO_2 and CH_4 emissions estimates are described above and occupy an area of 191 km^2 in the combined studied regions. This budget considers a 214 days open water season.

Authors	n	Boreal aquatic system type	CO_2 flux ($mg\ C\ m^{-2}\ yr^{-1}$)	CH_4 flux ($mg\ C\ m^{-2}\ yr^{-1}$)	Regional Lake CO_2 emission Tons of C	Regional Lake CH_4 emission Tons of C	Contribution of fluvial networks to total Aquatic CO_2 emission (%)	Contribution of fluvial networks to total Aquatic CH_4 emission (%)
This Study	46	Rivers and streams in Abitibi and James Bay, Canada	226 947	13 703	43 336	2 617	-	-
Juutinen et al., 2009	207	Finish lakes	-	588	-	2 251	-	54%
Huttunen et al., 2003	9	Finish lakes and reservoirs	49 449	1 293	189 133	4 945	19%	35%
Bastviken et al., 2004	13	Swedish lakes	-	640	-	2 447	-	52%
Duchemin et al., 1995	1	LaGrande Reservoir, Canada	69 978	482	267 650	1 842	14%	59%
Teodoru et al., 2012	1	Eastmain Reservoir (year 1), Canada	488 050	840	1 866 683	3 214	2%	46%
Korteleinen et al., 2006	207	Finish lakes	42 000	-	160 641	-	21%	-
Humborg et al., 2010	1 463	Swedish lakes	56 734	-	216 995	-	17%	-
Aufdenkampe et al., 2011	NA	Boreal lakes and reservoirs	130 000	-	497 221	-	8%	-
del Giorgio, unpublished data	88	Lakes in Abitibi and James Bay, Canada	66 694	959	255 089	3 667	15%	42%

Our study thus reinforces the notion that rivers play a disproportionate role in regional landscape CO_2 budgets (Aufdenkampe *et al.*, 2011, Humborg *et al.*, 2010, Jonsson *et al.*, 2007, Teodoru *et al.*, 2009) (Butman & Raymond, 2011, Dinsmore *et al.*, 2010), but more importantly, depicts riverine CH_4 emissions as an emerging component of the boreal landscapes carbon and greenhouse gas budgets. Using our own regional estimates in combination to river surface data provided by Bastviken et al. (2011), we have generated a first order calculation of CH_4 and CO_2 emissions from rivers and streams for the entire boreal biome. This exercise yield a potential total release of 0.02 Pg of CO_2-C annually, which agree very well with current estimates from Aufdenkampe et al. (2011) for the boreal biome. However, the same calculation for CH_4 yields total emissions by boreal rivers and streams of 1.46 Tg CH_4 yr^{-1} to the atmosphere, which is almost one order of magnitude above the current estimates for boreal fluvial CH_4 emissions of 0.2 Tg of CH_4 yr^{-1} (Bastviken *et al.*, 2011). This suggests that CH_4 emissions from fluvial networks in boreal landscapes may have been systematically underestimated. Although we acknowledge that the estimates from our lowland boreal regions do not necessarily represent the landscape heterogeneity of the boreal biome, our results undoubtedly show an unexpectedly high contribution of CH_4 to total fluvial GHG dynamics. This major role of streams and rivers emerges from the simultaneous measurements of CO_2 and CH_4 that we have performed on very large spatial and environmental gradients and suggest that CH_4 could account for more than a third of total fluvial GHG emissions in terms of CO_2 equivalent

CHAPITRE II

PATTERNS IN FLUVIAL pCO_2, pCH_4 AND GAS EXCHANGE ACROSS BOREAL RIVERS SUGGEST INCREASING FLUVIAL GREENHOUSE GAS EMISSIONS UNDER CLIMATE CHANGES

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2.2 Abstract

It is now widely accepted that boreal rivers and streams are regionally significant sources of CO_2 yet the role of these fluvial networks as CH_4 emitters, as well as the sensitivity of these emissions to climate change, are still largely unexplored. In this study, we explore the large-scale patterns of fluvial pCO_2, pCH_4 and gas exchange (k_{600}) relative to a set of key, climate-sensitive river variables across 46 streams and rivers in two distinct boreal landscapes of Northern Québec. We use the resulting models to determine the direction and magnitude of C-gas emissions from these boreal fluvial networks under scenarios of climate change. River pCO_2 and pCH_4 were positively correlated, although the latter was 2 orders of magnitude more variable. We provide evidence that in-stream metabolism strongly influences the dynamics of surface water pCO_2 and pCH_4, but whereas pCO_2 is not influenced by temperature, pCH_4 appears to be strongly temperature-dependent. The major predictors of ambient gas concentrations and exchange were water temperature, water velocity and DOC, and the resulting models indicate that total C-gas emissions (in CO_2 equivalent) from the entire network may increase between 12 and 64% under plausible scenarios of climate change over the next 50 years. These predicted increases in fluvial greenhouse gas emissions are mostly driven by steep increases in the contribution of CH_4 (from 36 to over 50% of total C-CO_2-equivalent emissions). The current role of boreal fluvial networks as major landscape sources of C is thus likely to expand, mainly driven by large increases in fluvial CH_4 emissions under the influence of global warming.

2.3 Introduction

Fluvial networks cover less than 0.5% of the land surface, yet they are increasingly recognized as significant components of the global climate system and C cycle (Aufdenkampe *et al.*, 2011, Bastviken *et al.*, 2011, Butman & Raymond, 2011). Rather than acting as passive pipes, receiving and transporting organic and inorganic C from the terrestrial landscapes to oceans, streams and rivers are dynamic conduits that simultaneously relocate soil CO_2 and CH_4 to the atmosphere, and generate CO_2 and CH_4 by consumption of terrestrial organic carbon (OC) (Cole *et al.*, 2007, Cole & Caraco, 2001, Tranvik *et al.*, 2009). Taken together, these two processes render fluvial networks as hot spots of CO_2 and CH_4 evasion, which are important greenhouse gases (GHG) (Butman & Raymond, 2011, Humborg *et al.*, 2010, Teodoru *et al.*, 2009). In the boreal biome, fluvial networks play a important role in the landscape GHG budget (Campeau *et al.*, submitted, Humborg *et al.*, 2010, Jonsson *et al.*, 2007, Teodoru *et al.*, 2009), as they drain the world's most extensive C reserves that are stored in soils and peatlands (Gorham, 1991, Meybeck, 1982). As a whole, the boreal biome occupies a central role in the current global C cycle and in the modulation of atmospheric GHG pools (Bonan *et al.*, 1992, Chapin *et al.*, 2000, Gorham, 1991), and is being subject to intense climatic warming (Flato & Boer, 2001). Major boreal C storages have all shown great sensitivity to the anticipated climate changes, e.g. forests (Bonan, 2008, Bond-Lamberty *et al.*, 2007), soils and

peatbogs (Gorham, 1991, Goulden *et al.*, 1998), and lakes (Benoy *et al.*, 2007, Gudasz *et al.*, 2010, Schindler *et al.*, 1996). As fluvial networks connect these different compartments within the boreal landscape, any potential changes in landscape C processing and exchanges will affect fluvial network properties and GHG emissions (Aufdenkampe *et al.*, 2011, Battin *et al.*, 2008, Battin *et al.*, 2009). Given the major role that fluvial networks play in regional C balances, it is important to be able to predict how this role may change under projected scenarios of climate shifts.

Climate change scenarios predict an increase in temperature and precipitation in most boreal regions, which will in turn result in increased overland and stream runoff (Clair *et al.*, 1998, Frigon *et al.*, 2010, Scinocca *et al.*, 2008, Solomon *et al.*, 2007). Despite uncertainties associated with predictions of climate change impacts on C balance in boreal landscapes (Davidson & Janssens, 2006, Gorham, 1991, Jarvis & Linder, 2000, Pastor & Post, 1988), there is indication that increasing annual temperature may stimulate biological activity enhancing CO_2 and CH_4 evasion to the atmosphere in both aquatic and terrestrial environments (Gudasz *et al.*, 2010, Perkins *et al.*, 2012), resulting in an erosion of the major OC pools (soils, peat, lake sediments). Similarly, increasing precipitation and runoff have been linked to enhanced OC export from terrestrial to fluvial networks (Clair *et al.*, 1999, Pastor *et al.*, 2003), increasing dissolved organic carbon (DOC) concentration in streams and rivers (Couture *et al.*, 2012, Eimers *et al.*, 2008, Erlandsson *et al.*, 2008), and also to increasing surface water C-gas concentrations (Jones *et al.*, 2003, Rantakari &

Kortelainen, 2005, Sobek *et al.*, 2005). Taken together, this information would suggest that climate shifts may result in increased C emissions from northern fluvial networks, but this prediction has never been explicitly explored.

In addition, most river studies have focused on possible responses in terms of CO_2. Methane emissions from soils, peatbogs, and lakes are now recognized as being extremely important regionally in boreal landscapes (Bartlett & Harriss, 1993, Bastviken *et al.*, 2011, Roulet *et al.*, 1997), yet CH_4 emissions from rivers have seldom been considered. Our own previous work, however, suggests that CH_4 emissions from northern rivers may be in the same order of magnitude as those from these other components of the boreal landscape (Campeau *et al.*, submitted), and yet we know little as to how these emissions may shift under scenarios of climate change. CO_2 and CH_4 emissions involve very different biological and physical pathways, and likely different environmental drivers as well, such that our understanding of the patterns and regulation of riverine CO_2 cannot simply be extrapolated to CH_4 dynamics. In this context, our objective was to explore the factors controlling these two processes individually but within the same systems, in the goal of developing the empirical tools that will allow us to predict how CO_2 and CH_4 fluxes may respond to climate-driven environmental changes.

There are two main components involved in determining fluvial GHG emissions: The patterns of gas partial pressure (pCO_2 and pCH_4) in surface waters, and also the physical features of gas exchange, reflected in the patterns in gas exchange coefficient (k). The former are linked to system metabolism and to inputs of

organic and inorganic C from the drainage basin. The latter expresses the rates of surface water equilibration with the atmosphere and is a mostly a function of stream hydrology and temperature (Macintyre *et al.*, 1995, Wallin *et al.*, 2011). Shifts in hydrologic regimes, for example, may affect gas fluxes both through their effect on C loading or processing (and thus on gas partial pressure), and on k through their impact on stream flow regime and turbulence, so these effects need to be quantified separately.

In this study, we have explored large-scale patterns in surface water pCO_2 and pCH_4, and also in k, as a function of climate-sensitive river properties, such as water temperature, water velocity and DOC concentration, in 46 rivers spanning a wide range of stream orders in two distinct lowland regions of boreal Québec. We further explore the direction and potential magnitude of change in these regional fluvial CO_2 and CH_4 fluxes, by applying the empirical models of pCO_2, pCH_4 and k to estimate under predicted scenarios of change in these climate-sensitive properties in Northern Quebec. In a companion paper (Campeau *et al.* submitted), we had carried out a large-scale spatial extrapolation of CO_2 and CH_4 fluxes to estimate total C emissions from the fluvial network in these two boreal regions of Quebec, which we used, in combination with the developed empirical models of pCO_2, pCH_4 and k to quantify the projected changes in total fluvial C emissions in the region.

2.4 Materials and methods

2.4.1 Sampling location and schedule

We sampled a total of 46 different rivers and streams, within two neighboring lowland regions of northern Québec, Canada: Abitibi (47-48°N, 78-79°W), and James Bay (48-49°N, 78-79°W), where 31 and 15 different sites were sampled respectively (Figure 2.1). The streams and rivers were selected in order to incorporate the full spectrum of stream and river size in each region, ranging from stream order 1 to 6, and to be part of distinct watersheds for a comprehensive representation of the regional landscapes. Sampling was carried out at four specific periods during the open-water period between May 2010 and May 2011 (in June, July/August and October of 2010 and May 2011), corresponding to major seasonal variations in temperature and precipitation. All sites were sampled once in mid-summer (July/August 2010), 32 of these sites were additionally sampled in early summer and in autumn (end of May/June 2010 and October 2010 respectively), and 13 of these were also sampled in spring (early-May 2011). In these northern Quebec regions, summers are short and warm with temperatures peaking in July, while winters are cold with the lowest temperatures in January (Table 2.1). Peak stream flows typically occur twice a year, once at spring thaw (April-May), and once in autumn (September-October) due to increased precipitation, while base-flow occurs in mid-summer and during winter. The summer of 2010 was significantly dryer (50% less) than the long-

term annual averages, whereas autumn (September 2010) and spring (April 2011) received twice as much rain compared to annual averages (Table 2.1).

The two regions visited in this survey differ in terms of their plant coverage and soil composition, but both share an extremely flat topography (average elevation of 300 m ± 31SD), a dense aquatic coverage (representing 15-22% of total catchment area, respectively) and a similar climate (Table 2.1). The regional surface water distribution differs in the two regions, whereas larger lakes dominate the Abitibi region, the James Bay region is characterized by many small lakes and extensive wetlands (Table 2.1 and Figure 2.1). Fluvial networks in both regions are extensive and complex, following a trellis and dentritic drainage pattern, typical to lowland regions. Low order streams (1 to 3) in Abitibi are intensively affected by beaver impoundments, which strongly influence the hydrological regimes (Naiman *et al.*, 1988). In contrast, beaver populations are small in the James Bay region because of the sparse broadleaf forests coverage and as a result, beaver impoundments on streams are essentially absent in that region.

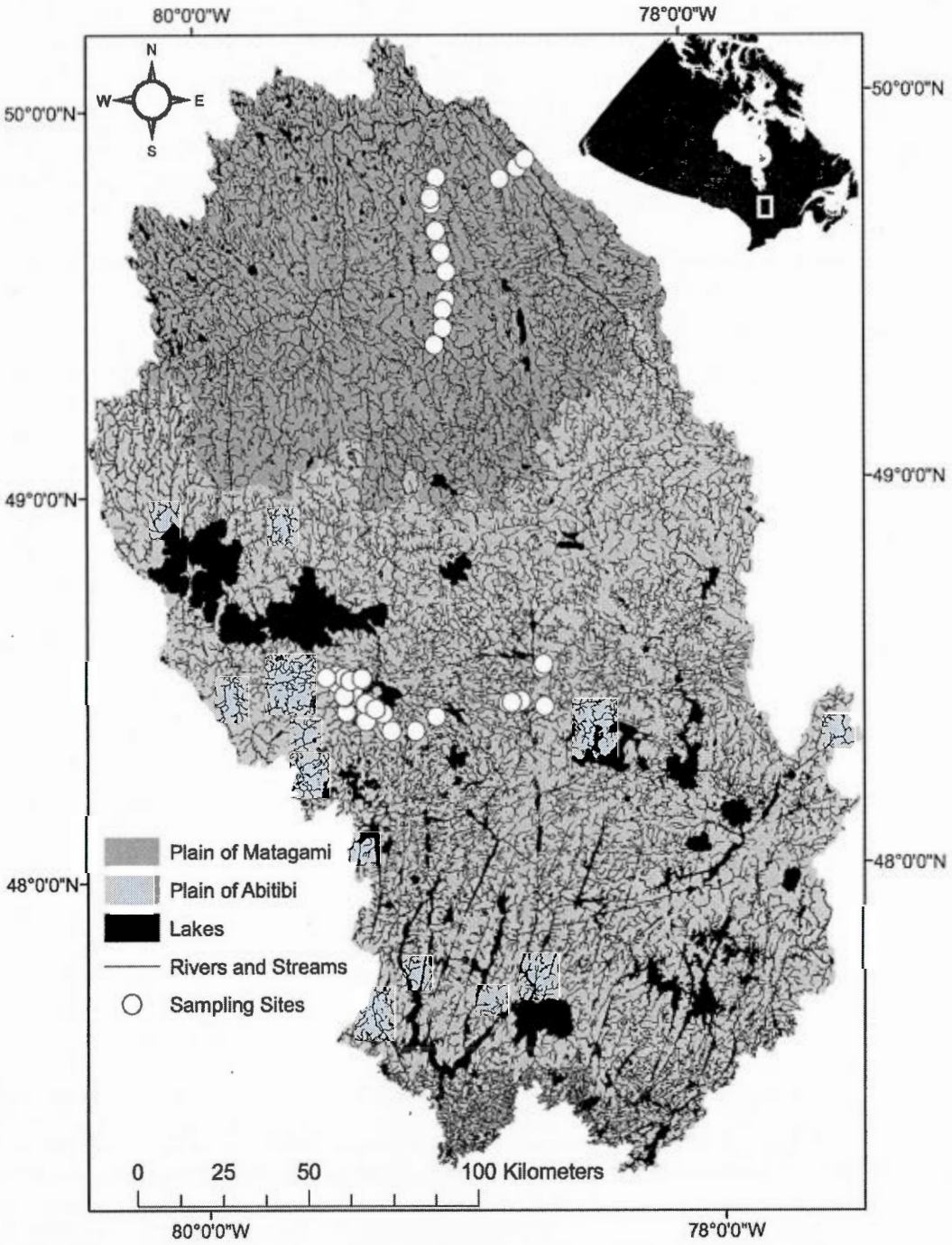

Figure 2.1: Map showing the distribution of sampled rivers and streams within the two studied regions, Abitibi and James Bay.

Table 2.1: Landscape and climatic properties for the Abitibi and James Bay regions.

Region	Area (km^2)	Forested coverage	Dominant tree species	Dominant surficial soil deposit (%)	Inland water coverage (%)	Annual temperature (C°)	Annual precipitation
Abitibi	30 418	Coniferous (26%) Broadleaf (61%) Mixed wood (13%) Shrub land (10%)	balsam fir (*Abies balsamea*) white birch (*Betula papyrifera*) white spruce (*Picea glauca*) american aspen (*Populus tremuloides*)	Clay (50%) Till (25%) Roc (17%) Sand (4%).	Lakes (11%) Wetlands (3%) Fluvial (0.5%)	Average 0.7 Maximum 16.7 Minimum -17.9	Rain 700 mm Snow: 250 cm total 950 mm
James Bay	13 790	Coniferous (67%) Broadleaf (30%) Mixed wood (3%) Shrub land (11%)	black spruce (*Picea mariana*) Undergrowth: mosses (*Hypnaceae*) shrubs (*Ericaceae*)	Organic (95%) Clay (5%)	Lakes (3%) Wetlands (18%) Fluvial (0.4%)	Average -0.7 Maximum 16.0 Minimum -20.0	Rain 618 mm Snow 314 mm total 905 mm

2.4.2 Surface water C-gas concentration and atmospheric fluxes

Surface water partial pressures of CO_2 (pCO_2) and of CH_4 (pCH_4) were measured using the headspace method, and pCO_2 was measured in situ with a PP Systems (Model EGM-4) infrared gas analyzer, whereas pCH_4 samples were stored in 25-ml glass vials equipped with crimped rubber stoppers for subsequent analysis in laboratory with Shimadzu GC-8A Gas chromatograph with FID (flame ionization detector) (Campeau *et al.*, submitted). Atmospheric CO_2 and CH_4 fluxes (mmol m^{-2} d^{-1}) across the air-water interface were determined with a 16L floating chamber (0.09 m^2) (Vachon *et al.*, 2010). For the determination of CO_2 fluxes, the ambient pCO_2 in the chamber was recorded with model EGM-4 connected to the chamber via an enclosed re-circulating system, while a similar system allowed to withdraw, after 0, 5 and 10 minutes, 30 ml of the chamber's headspace for analysis of ambient pCH_4 (Campeau *et al.*, submitted). The ensuing rates of CO_2 and CH_4 exchange were used to estimate fluxes, f_{CO2} and f_{CH4} (mmol m^{-2} d^{-1}), with the following equation;

$$F_{CO_2} = \left(\frac{s * V}{mV * S} \right) * f \qquad (2.1)$$

Where (s) is the accumulation rate of gas in chamber (µatm min^{-1}); (V) is the chamber's volume (L); S is the chamber's surface area (m^2); (mV) (molar volume) is the volume of one mole of gas at the current atmospheric pressure (L mol^{-1}); and (f) is a conversion factor from minutes to day (1d = 1 440 min).

CO_2 exchange between surface water and the atmosphere occurs strictly by diffusive process, whereas CH_4, may also be transferred to the atmosphere via ebullitive (Bastviken *et al.*, 2004, Mattson & Likens, 1990) and micro-bubbling fluxes (Prairie & del Giorgio, 2013). As a result, we used fCO_2 to estimate a strictly diffusive gas transfer velocity (k_{CO2}), by inverting equation for Fick's law of gas diffusion as shown by the following equation;

$$k_{CO_2} = \frac{F_{CO_2}}{Kh(pCO_{2water} - pCO_{2air})} \quad (2.2)$$

where k_{CO2} is the gas transfer velocity in m d^{-1} specific for CO_2; fCO_2 is the measured CO_2 flux between the surface water and the atmosphere in the floating chamber, kH is Henry's constant adjusted for salinity and temperature and ΔpCO_2 is the difference between CO_2 partial pressure in the surface waters and the atmosphere (µatm). We standardized k_{CO2} to Schmidt number 600 (k_{600}) with the following equation; (eq.4)

$$k_{600} = k_{CO2} * \left(600/Sc_{CO2}\right)^{-n} \quad (2.3)$$

where Sc_{CO2} is the CO_2 Schmidt number at a the stream water temperature (Wanninkhof, 1992), n was fixed at 2/3 which corresponds to a wind speed of <3,7m s^{-1}(Guérin *et al.*, 2007). We then used this k_{600} to estimate the strictly diffusive CH_4 and from its difference from actual flux measured in the chambers, we were able to derive the non-diffusive CH_4 flux.

2.4.3 River and stream properties

We measured ambient water temperature (°C), dissolved oxygen (mg L^{-1}) pH and conductivity with a environmental monitoring probe (YSI, Model 600XLM) equipped with a rapid pulse DO probe. Measurements were taken 0.1 m below the surface, and water was collected at the same location for subsequent analyses. Channel width was measured directly at the cross section of the sampling location or indirectly via satellite images for the largest rivers (stream order 6). Channel depth was measured at the center of the channel and at several discrete points across the channel (between 1 to 5 depending on the width of the channel). Water velocity was measured at each of these discrete points across the channel with a Flow tracker ADV (Acoustic Doppler Velocimeter) and used in combination to the stream width and depth to estimate discharge (Q) (m^3 s^{-1}) according The Mid Section Discharge Equation Method (U.S. Geological Survey (USGS)). The latter measurements were not possible to record for largest rivers of stream order 6. DOC concentration (mg C L^{-1}) was measured from 0.45μm-filtered water samples with a Total Organic Carbon Analyzer, TOC1010 - OI Analytical (precision of 0.05 mg C L^{-1}) prior to sodium persulfate digestion of the sample.

2.4.4 Statistical analysis

We performed a series of simple linear regressions to explore the patterns of pCO_2, pCH_4 and k_{600} and their relationship to climate-sensitive stream properties (e.g. water temperature, DOC concentration, stream flow). Data were log-transformed to satisfy assumption of residuals normal distribution and homoscedasticity. We also carried out multiple regression analyses to determine the most effective models, and used these to simulate changes in pCO_2, pCH_4 and k_{600} under scenarios of potential climate changes.

2.5 Results

Surface water pCO_2 and pCH_4 were highly variable within the fluvial networks in both Abitibi and James Bay regions, but systematically super-saturated with respect to the atmosphere, ranging 2 orders of magnitude for pCO_2, and 4 orders of magnitude for pCH_4 (Table 2.2). The average pCO_2 did not vary significantly between regions ($p=0.07$) or seasons ($p=0.09$) (Table 2.2). Likewise, pCH_4 was not statistically different between regions ($p=0.16$), but differed significantly on a seasonal basis ($p=0.002$) (Table 2.2). The gas transfer velocity (k_{600}) in the fluvial network of Abitibi and James Bay was typically low, and did not vary across regions ($p=0.9$) but did vary significantly ($p<0.0001$) across seasons, with highest values observed during spring and autumn, at high flow periods (Table 2.2).

Table 2.2 Summary table of surface water pCO_2, pCH_4 and gas exchange coefficient (k_{600}), for the open water period, individual seasons and Abitibi and James Bay regions

	All Sites			Spring	Summer	Autumn	Abitbi	James Bay
n	134			13	89	32	104	30
	average	min	max	average	average	average	average	average
pCO_2 (uatm)	2 959	509	10 537	2 082	3 202	2 640	3 125	2 384
pCH_4 (uatm)	1 781	24	28 683	177	2 600	284	2 031	923
k_{600} ($m\ d^{-1}$)	1.11	0.1	6.68	2.11	0.68	1.65	1.10	1.14

2.5.1 Patterns of fluvial pCO_2 and pCH_4

We observed a significant relationship between the average surface water pCO_2 and pCH_4, suggesting that fluvial pCO_2 and pCH_4 may share similar sources and drivers across large spatial and temporal gradients. (Figure 2.2):

$$\text{Log } pCH_4 = -4.93 + (2.27 \text{ Log } pCO_2) \qquad r^2 = 0.57 \qquad n=128 \ (p<0.0001) \qquad (2.4)$$

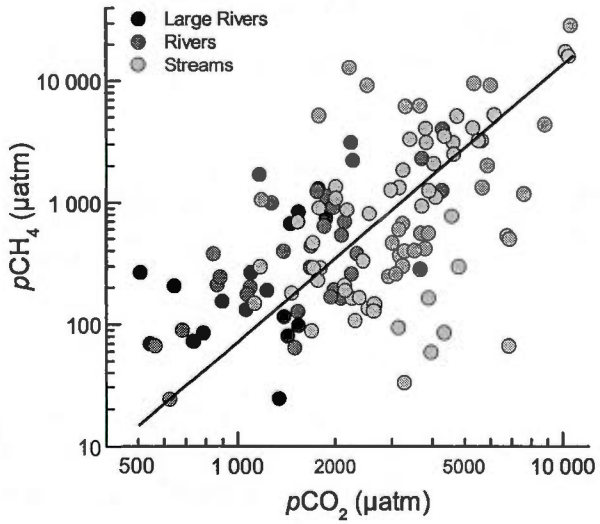

Figure 2.2: Relationship between average surface water pCO_2 and pCH_4 for all the sites and sampling dates throughout the ice-free season (May to October). Stream orders 5-6 are identified as large rivers while stream order 3-4 and 1-2 are identified as rivers and streams, respectively. The data have been log-transformed and the line represents the orthogonal regression (Equation 2.4).

In particular, both gases appeared to be related to in situ metabolism, albeit differently. There was a significant negative relationship between CO_2 departure and O_2 departure from atmospheric saturation, both expressed in moles (Figure 2.3a).

O_2 dep = -78.01 - (0.77 * CO_2 dep) r^2=0.66 n=135 (p<0.0001) (2.5)

Similarly, there was a negative relationship between CH_4 departure and O_2 departure from atmospheric saturation, both expressed in moles. However, the relationship was nonlinear and rather followed a semi-power relationship (Figure 2.3b):

O_2 dep = -165.94 - (111.23 * Log CH_4 dep) r^2=0.65 n=128 (p<0.0001) (2.6)

Stream waters were systematically above anoxic levels (below - 420 uM), indicating that elevated methane concentrations can nonetheless be found in oxic river waters (Figure 2.3b). This relationships suggests that at least a portion of the ambient CO_2 and CH_4 supersaturation may result from in situ metabolism, yet these links and pathways are likely different for CO_2 and CH_4.

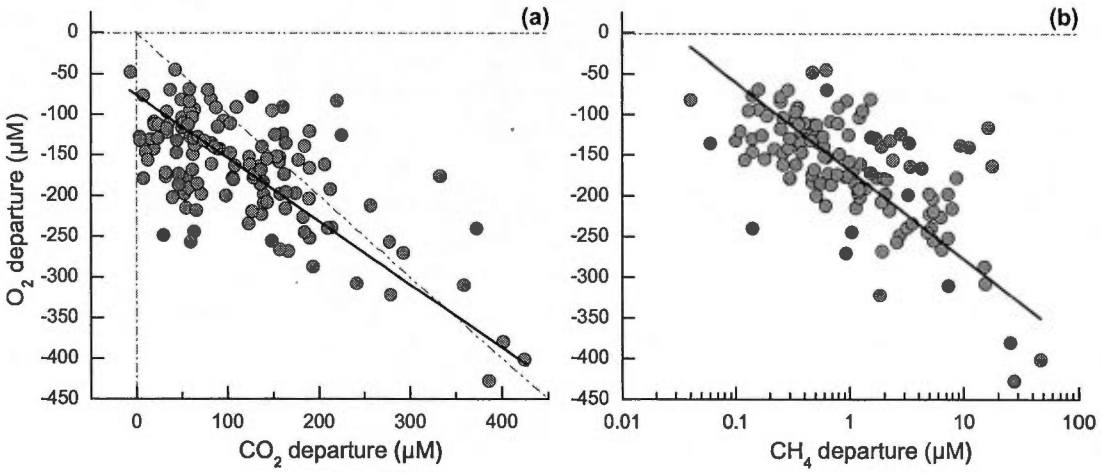

Figure 2.3: Relationship between O_2 departure from saturation (µM) and (a) CO_2 departure from saturation (µM), and (b) CH_4 departure from saturation (µM). The C-gases are systematically well above atmospheric saturation (on the right hand side of the vertical dotted line) while oxygen is consistently below saturation (bellow horizontal dotted line). The slope (-0.77) of the least squares relationship shown in figure 2a (full line) is relatively close to the 1:1 slope (bold dotted line) (Equation 2.5). The slope (-111.23) of the least squares relationship shown on figure 2 (b) is a semi-power function (Equation 2.6). Open circles represent the sites in the James Bay region and the gray circles represent the sites in the Abitibi region.

2.5.2 Relationships with temperature

We further tested the individual response of surface water pCO_2, pCH_4 and k_{600} to potential drivers that may be affected by climate change: water temperature, stream flow and DOC, with the aim of using the resulting models to assess the sensitivity of fluvial CO_2 and CH_4 emissions to climate change. There was no significant relationship between pCO_2 and water temperature ($p=0.09$), but we did observe a highly significant positive relationship between pCH_4 and water temperature (°C) (Figure 2.4 a):

$$\text{Log } pCH_4 = 1.86 + (0.06\ T°_{water}) \qquad r^2=0.31\ n=129 \qquad (p<0.0001) \qquad (2.7)$$

As a result, there was a significant positive relationship between the contribution of CH_4 on total carbon gas (TCG) concentration ($CO_2 + CH_4$ expressed as mg C L^{-1}) and water temperature (°C) following a positive semi-log relationship (Figure 2.4 b):

$$\text{Log } CH_4/TCG = -2.90 + (0.06\ T°_{water}) \qquad r^2=0.39\ \ n=128\ (p<0.0001) \qquad (2.8)$$

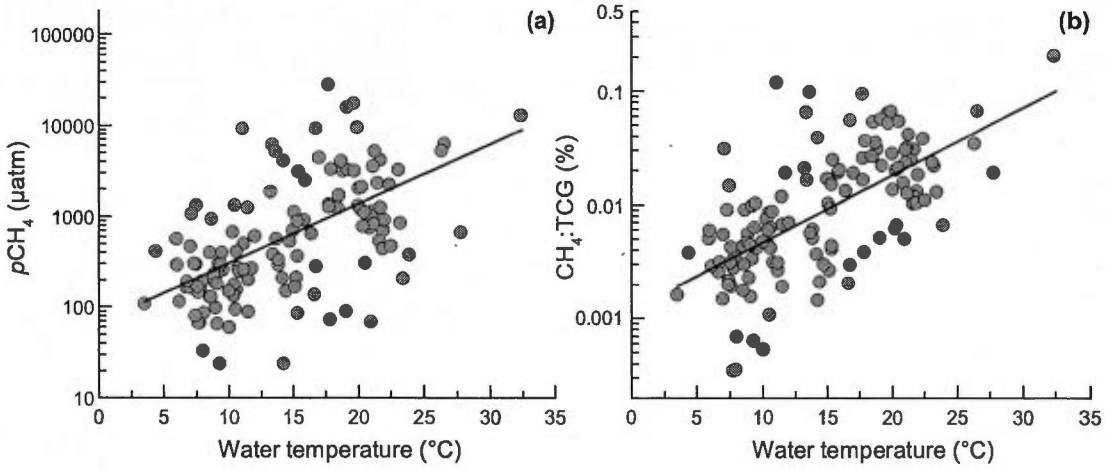

Figure 2.4: The relationship between water temperature (°C) and (a) surface water pCH_4 (a), and (b) the ratio of mass of CH_4: total C-gas mass (TCG, in mg of C). Data are displayed on semi-logarithmic scales (Equations 2.7 and 2.8).

2.5.3 Relationships with hydrology

In lowland regions such Abitibi and James Bay, fluvial networks are characterized by overall very slow stream flow, particularly in the smallest streams that have the lowest discharge. In this regard, there was a positive orthogonal relationship between discharge ($m^3\ s^{-1}$) and stream velocity ($m\ s^{-1}$) across the range of stream orders and seasons:

$$\text{Log } \upsilon = 0.65 + 0.62 \text{ Log } Q \qquad r^2=0.69 \qquad n=105 \qquad (p<0.0001) \quad (2.9)$$

This contrasts with regions of higher elevation and slope, where water velocity is generally greater in small streams, and declines in large rivers with increasing discharge. We observed a significant negative (log-log) relationship between pCO_2 and pCH_4 as functions of water velocity ($p<0.0001$) (Figure 2.5 a and b):

$$\text{Log } pCO_2 = 3.12 - (0.21 \text{ Log } \upsilon) \qquad r^2=0.31 \qquad n=99 \qquad (p<0.0001) \quad (2.10)$$

$$\text{Log } pCH_4 = 2.19 - (0.42 \text{ Log } \upsilon) \qquad r^2=0.26 \qquad n=96 \qquad (p<0.0001) \quad (2.11)$$

The k_{600} tended to increase along this same gradient of stream water velocity, (Figure 2.5 c)

$$\text{Log } k_{600} = 0.18 + (0.27 \text{ Log } \upsilon) \qquad r^2=0.22 \qquad n=89 \qquad (p<0.0001) \quad (2.12)$$

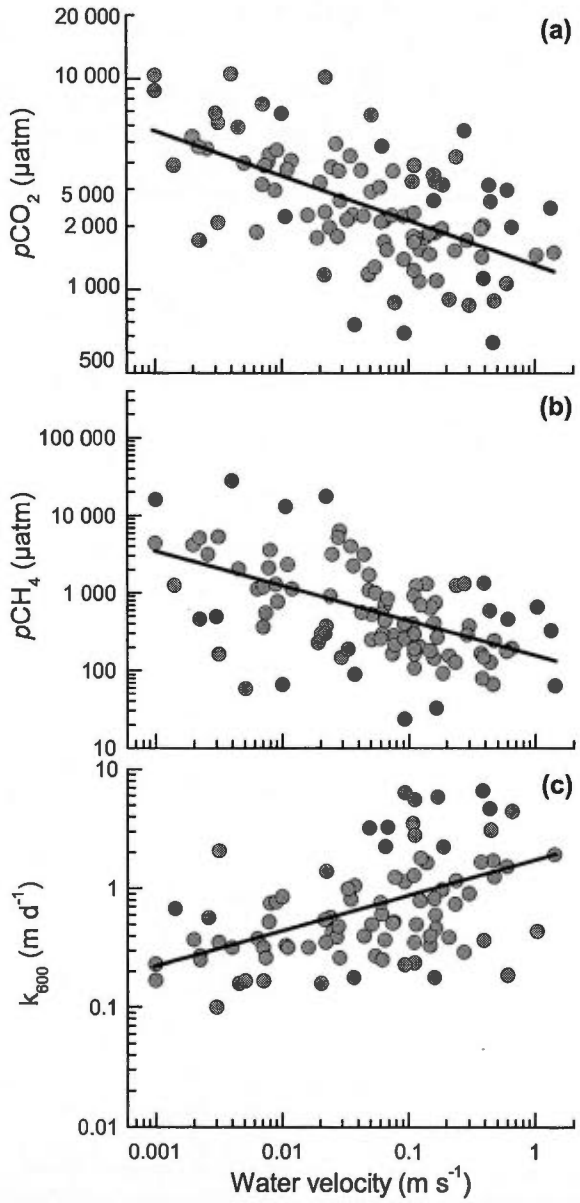

Figure 2.5: The relationship between water velocity (m s^{-1}) and (a) surface water pCO_2 (µatm), (b) surface water pCH_4 (µatm), and (c) the gas exchange coefficient (k_{600}, m d^{-1}). All data are log-transformed, and the lines represent the least square regression fits (Equations 2.10, 2.11 and 2.12).

2.5.4 Relationship with DOC concentration

DOC concentrations within the fluvial network ranged from 3.9 to 52.6 mg/L and were significantly different between the two regions ($p<0.0001$), averaging 16.4 and 33.6 mg L^{-1} in Abitibi and James Bay, respectively. DOC concentrations also varied significantly between seasons ($p=0.008$), with lowest values following the spring thaw (14.5 mg C L^{-1}) and highest in summer (17.7 mg C L^{-1}) and autumn (24.5 mg C L^{-1}). We did not find any significant patterns between DOC and pCO_2 ($p=0.13$) or pCH_4 ($p=0.68$) in either of the two regions nor within seasons.

2.5.5 Multiple regression models of stream gas concentration

We performed multiple regression analyses to assess the combined the effect of the above climate-sensitive variables on river CO_2 and CH_4 dynamics. The predictive model for pCO_2 included DOC concentration and water velocity as independent variables:

$$\text{Log } pCO_2 = -2.76 + (0.28 \text{ Log DOC}) - (0.22 \log \upsilon) \quad r^2 = 0.38 \; n=91 \; (p<0.0001) \tag{2.13}$$

The best combined predictive model for pCH_4 also included DOC and water velocity, in addition to temperature:

$$\text{Log } pCH_4 = -0.59 + (0.70 \text{ Log DOC}) - (0.25 \log \upsilon) + (0.06\ T^{\circ}_{w})$$

$$r^2 = 0.54 \quad n=88 \quad (p<0.0001) \qquad (2.14)$$

It is interesting to note that whereas DOC was not significantly related to either pCO_2 or pCH_4 individually, it was highly significant in both multiple regression models once velocity was included (p=0.006 for pCO_2, and p=0.0003 for pCH_4).

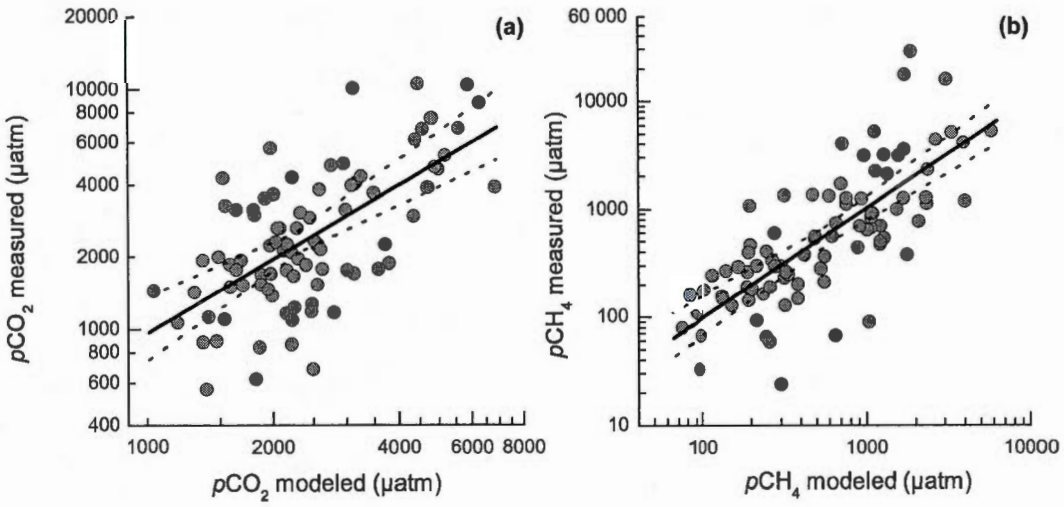

Figure 2.6: The relationship between measured and predicted values from the multiple regression models for (a) surface water pCO_2, and (b) surface water pCH_4. All data are log-transformed, and the lines represent the least square regression fits (Equations 2.13 and 2.14).

2.6 Discussion

2.6.1 Drivers of fluvial pCO_2 and pCH_4

Boreal rivers and streams connect various landscape compartments and simultaneously play the double role of pipes, channeling soil-derived CO_2 and CH_4 to the atmosphere, and as reactors, generating CO_2 and CH_4 from the degradation of terrestrially-derived organic carbon (Aufdenkampe *et al.*, 2011, Battin *et al.*, 2008). These combined terrestrial and aquatic processes shape surface water pCO_2 and pCH_4 in rivers and streams, which are, not surprisingly, extremely variable across spatial and temporal gradients. In the Abitibi and James Bay regions, surface water pCH_4 ranged more than 4 orders of magnitude across rivers (Table 2.2), which was much more variable than pCO_2, which still ranged over 2 orders of magnitude.

Despite this high variability, surface water pCO_2 and pCH_4 were positively related to each other, across the fluvial networks and along the different seasons (Figure 2.2), suggesting a level of common regulation for both gases, at least at the whole network scale. The only previous study to report a significant co-variation between CO_2 and CH_4 is that by (Richey *et al.*, 1988) for the Amazon river, although this pattern can be inferred from data presented by (Billett & Harvey, 2012, Billett & Moore, 2008) for temperate streams in peat-dominated catchments, and by (Huttunen *et al.*, 2003, Repo *et al.*, 2007) for boreal lakes. This is rather surprising, considering that the production of both gases is associated to different environmental drivers, metabolic pathways and even spatial locations.

It is possible that this relationship reflects a common origin of at least a portion of the ambient CO_2 and CH_4. In this regard, we observed a negative relationship between both CO_2 and CH_4 with O_2 (both expressed as departure from saturation, Figure 2.3), which we interpret as evidence that there is a local metabolic component that plays a major role in the dynamics of both gases (e.g. respiration, methanogenesis, methane oxidation). The pattern of surface CO_2 and O_2 has been reported for other aquatic ecosystems (Del Giorgio *et al.*, 1999, Kortelainen *et al.*, 2006, Richey *et al.*, 1988), and it has been interpreted as reflecting the pelagic respiratory production of CO_2. The pattern of surface CH_4 and O_2, on the contrary, has not been previously reported, and its interpretation is less straightforward, because CH_4 is thought to be mostly produced in anoxic sediments and not in the water column (Bastviken *et al.*, 2004, Dahmn *et al.*, 1991(Thauer & Shima, 2006). This relationship may rather indicate that CH_4 tends to be high in environments that have overall high rates of heterotrophic metabolism, which is reflected in low surface water O_2 concentrations.

The relative influence of in situ metabolism on these gases can be further inferred from the degree of coupling between the two: Sites that were characterized by high CH_4 were systematically highly supersaturated in CO_2, and vice versa. There were sites or times, however, when CO_2 was high but CH_4 was low, yet the reverse never occurred (Figure 2.2), suggesting that at low levels of river metabolism, other sources and pathways may become important for CO_2 but less so for CH_4. That river metabolism plays a stronger role on CH_4 dynamics than it does on CO_2 is further

reflected in the much tighter relationship between O_2 and CH_4 departure relative to O_2 and CO_2 departure (Figure 2.3).

The link of CH_4 to metabolism is also reflected in the strong apparent temperature dependency of pCH_4 that we observed (Figure 2.4). Temperature has been shown to strongly modulate CH_4 concentrations in a wide range of aquatic environments, from streams (Billett & Moore, 2008), lakes (Huttunen *et al.*, 2003), wetlands (Macdonald *et al.*, 1998), and boreal soils (Ullah & Moore, 2011). The temperature effect on CH_4 concentration was equivalent to a temperature coefficient (Q_{10}) of 4.1, which is within the range of published values from boreal wetlands; 2.2 to 4.8 (Macdonald *et al.*, 1998) and 0.6 to 12 (McKenzie *et al.*, 1998). In contrast, we did not find a significant relationship between temperature and CO_2, and this agrees with previous studies for rivers (Dawson *et al.*, 2009) and lakes (Sobek *et al.*, 2005), again possibly reflecting the diversity of pathways that deliver CO_2 to these rivers. The strong link to temperature and metabolism explain the much stronger seasonality that we observed in CH_4 relative to CO_2 (Table 2.2).

Another potential indication of links to local metabolism is the fact that both pCO_2 and pCH_4 were positively related to DOC, but again the relationship was stronger for CH_4. Many studies have reported a positive relationship between DOC and pCO_2 for lakes (Jonsson *et al.*, 2001, Lapierre & del Giorgio, 2012, Sobek *et al.*, 2005), which has been interpreted as DOC acting as a substrate for the production of CO_2 in the water column. It is interesting then to note that CH_4 and DOC were positively related, as the connection between surface water DOC concentration and

sediment CH_4 fluxes in lakes or rivers is not obvious, although it may be mediated by DOC flocculation to the bottom of lakes and rivers, where it may fuel methanogenesis. It should be pointed out that DOC emerged as significant only when combined with water velocity in a multiple regression model for both CO_2 and CH_4 (Figure 2.6 and Equation 2.13 and 2.14). Since velocity is itself is related to discharge (Equation 2.9) this would suggest that the production of CO_2 and CH_4 on the basis of DOC might result from the interplay between the amount of DOC loaded into these rivers and its hydrological retention within the system.

These results further confirm that, as opposed to pCH_4, river pCO_2 has a large external determinant, likely related to groundwater inputs of soil-derived CO_2. For example, the slope of the relationship between CO_2 and O_2 departure was above one (Figure 2.3a), which suggests additional CO_2 input relative to strictly metabolic production. Likewise, the smallest streams in our study were essentially spring fed, and these were consistently supersaturated in CO_2 but roughly at equilibrium relative to O_2 and CH_4 (see Figure 2.3a). Finally, the seasonal variability of pCO_2 was greatly dampened relative to that of pCH_4 (Table 2.2), suggesting a relatively constant supply of CO_2 throughout the year, regardless of the patterns of in situ metabolism. The relative importance of in situ versus external inputs of CO_2 not only likely varies with river order and total metabolism, but also on a seasonal basis, for example, during warm base-flow periods when metabolism dominates, or during cold high-flow periods like spring and autumn when soil-derived CO_2 inputs would dominate.

2.6.2 Role of hydrology on C-gas concentrations and fluxes

Carbon-gas concentrations are typically negatively related to hydrological parameters, such as discharge, velocity, turbulence (Weyhenmeyer *et al.*, 2012), and there are several underlying processes that may contribute to these patters: The enhancement of atmospheric gas evasion via increasing discharge and resulting turbulence (Dawson *et al.*, 1995, Genereux & Hemond, 1992, Teodoru *et al.*, 2009); gas dilution with increasing river flow (Dinsmore & Billett, 2008, Hope *et al.*, 2004, Wallin *et al.*, 2010); reduction of aquatic C-gas production in fast flowing rivers (Battin *et al.*, 2008, Dawson *et al.*, 2009). In the Abitibi and James Bay region, we observed that both pCO_2 and pCH_4 declined with increasing water velocity, and that gas exchange coefficients (k_{600}) increased along the same velocity gradient (Figure 2.5). As a result, there was a significant negative relationship between pCO_2 and k_{600} ($p<0.0001$), and also between pCH_4 and k_{600} ($p=0.0003$), which suggests that the dominant mechanism underlying the declining C-gas concentration with water velocity could be the increased vertical gas loss to the atmosphere. We further explored this possibility by regressing the residuals of the pCO_2 vs k_{600} (and also of pCH_4 vs k_{600}) and observed that these residuals still had a significantly negative relationship with water velocity ($p=0.0006$ and $p=0.0002$, respectively), suggesting that the physical enhancement of atmospheric gas loss by the increasing water velocity was not the only underlying mechanism for the patterns in pCO_2 and pCH_4. Since discharge and water velocity are positively correlated to each other in these

regions of flat topography (Equation 2.9), we further tested if the influence of water velocity on C-gases may in part be due to the concomitant increases in discharge. We calculated the residuals of the relationship between discharge and water velocity represented by equation 2.9, and observed that these were negatively related to both pCO_2 ($p=0.01$) and pCH_4 ($p < 0.0001$). This would indicate that for a given water discharge, increasing water velocity will tend to lower the pCO_2 and pCH_4 significantly, and that decline of surface water C-gas concentration with increasing water velocity was not caused by gas dilution with the increasing river flow. We propose that one of the major mechanisms responsible for the decrease of pCO_2 and pCH_4 with increasing water velocity is the loss of biophysical opportunities where biogenic C-gas production can occur within the fluvial network. Rapid stream flow can restrain the settlement of biofilm and aggregates in the water column (Battin *et al.*, 2008), the flocculation of DOC and POC on the riverbed (Jones, 1995, Mulholland, 1981) and also reaeration rates and other properties of the riverbed where methanogenesis mainly occurs (Hlavacova *et al.*, 2006). In this regard, we can speculate potential shifts in stream flow in response to climate changes could have an affect C-gas fluxes, through its simultaneous influence on gas exchange and also the C-gases production in the fluvial network.

2.6.3 Shifts in stream properties resulting from projected climate changes

The increased awareness of the role of fluvial networks on regional C balances has led to a surge in the number of studies investigating the drivers and controls of river CO_2 and CH_4 fluxes, yet the potential responses of fluvial GHG emissions to climatic shifts remains largely unexplored. Our results suggest that the modulation of CO_2 and CH_4 fluxes by climate-sensitive stream properties is complex, and combines several mechanisms involving thermal, hydrological and biological effects. Not only do these results confirm the existence of potential feedbacks between fluvial C fluxes and climate, but they also allow us to determine the direction and potential magnitude of changes in fluvial CO_2 and CH_4 emissions as a response to these projected environmental changes (Figure 2.6). Although there appears to be common drivers linking surface water pCO_2 and pCH_4 in fluvial networks, there are also some major differences in the regulation of these gases that may result in very distinct response to climate change, and these responses need to be addressed separately.

Scenarios of climate change vary greatly among regions, including a wide range of possible increases in temperature, combined with increasing or declining annual precipitations and runoff (Friedlingstein & Prentice, 2010, Scinocca *et al.*, 2008, Solomon *et al.*, 2007). These region-specific scenarios of climate change must be taken into account to model the potential response and alteration of fluvial properties. In the Abitibi and James Bay regions, climate change scenarios suggest an

overall increase of summer air temperature of 3-4 °C (±0.4°C), and annual precipitation (de Elia & Coté, 2010), resulting in a widespread intensification of the overland and stream runoff by 12% (±8%) within the next 30 to 50 years (Clair *et al.*, 1998, Frigon *et al.*, 2010). We estimated the changes in stream properties (water temperature, water velocity and DOC concentration) on the basis of these regional predictions, and used these in turn to further assess the likely direction and magnitude of changes in fluvial CO_2 and CH_4 fluxes.

We estimated the magnitude of the anticipated increase of average water temperature, using the empirical relationship between air-temperature and water temperature based on our own field measurements:

$$T°_{water} = 4.15 + 0.536 * T°_{air} \qquad r^2 = 0.34 \qquad n=114 \qquad p<0.0001 \qquad (2.15)$$

Water velocity is partly a function of stream discharge (Equation 2.9) (Govers, 1992), we used a range of projected increase in runoff and stream discharge by (Frigon *et al.*, 2010) to estimate a realistic increase in average stream velocity for the region. Runoff intensification has been frequently associated with increasing terrestrial OC export and rising DOC concentration (Couture *et al.*, 2012, Mulholland, 1997, Tranvik & Jansson, 2002), although empirical models to quantify this impact are lacking, possibly because specific climatic and geological properties also modulate C transfers from terrestrial to aquatic environments (Laudon *et al.*, 2012). As a result, we chose to apply a large but realistic range of increases in DOC

concentration associated to specific scenarios of climate change (Table 2.3). A summary of projected changes in stream properties, which were used to simulate the impact of climate change on fluvial C fluxes is presented in Table 2.3, where the minimal changes are represented in Scenario A and maximal changes in Scenario C.

Table 2.3: Summary table of predicted changes in stream properties in response to climate changes scenarios for the next 30 to 50 years in the two studied regions, used for simulating the influence of climate changes on fluvial C fluxes

Climatic Properties		Scenario A	Scenario B	Scenario C
Runoff *	(% change)	6	12	18
Air Temperature **	(°C)	3.0	3.5	4.0
Open water period	(days +184)	190	196	202
Stream Properties				
Water Temperature	(°C)	1.6	1.85	2.1
Water Velocity	(% change)	1	7.4	11
DOC concentration	(% change)	11	33.5	78

*Based on (Clair *et al.*, 1998, Frigon *et al.*, 2010)
**Based on (de Elia & Coté, 2010)

2.6.4 Simulated change in fluvial pCO_2, pCH_4 and gas exchanges.

We used the three multivariate empirical models developed in the results section to predict pCO_2, pCH_4 and k_{600} under simulated conditions of water temperature, velocity and DOC concentration, respectively, projected for the coming 30 to 50 years (Table 2.3). The outcome of this simulation is a dramatic increase in surface water pCH_4 (34 to 92%), largely exceeding the predicted increase of surface water pCO_2 (2 to 14%) (Table 2.4). This divergence is partially caused by the much higher apparent temperature-sensitivity of pCH_4 compared to that of pCO_2 (Figure 2.3), but also by the stronger influence of increasing DOC on pCH_4 (Equation 2.14). Increases in DOC concentration were responsible for about half of the observed response of pCH_4 in every simulated scenario, with the remaining half being caused by increasing water temperature. This indicates that pCH_4 is highly influenced by climatic divers through both the direct influence of increasing temperatures, and indirectly through increased runoff and DOC loading, whereas pCO_2 is weakly impacted by those changes.

An increase of at least 37% in fluvial DOC concentration was required to produce a significant (>6.5%) increase in average pCO_2 (Table 2.4). This level of increase in DOC, however, is well within the predicted range of DOC change in a variety of northern landscapes. Couture et al. (2012) have reported a rate of increase of 0.05 mg C L^{-1} yr^{-1} over the past decades in central and northern Québec, which translates into a 50% increase in average DOC within the next 50 years. Likewise,

Eimers et al. (2008) reported a 52 to 78% increase in DOC concentration in neighboring regions of northern Canada, whereas a 65% increase is projected in boreal Norwegian lakes and rivers (Larsen *et al.*, 2011). In this regard, the increase of surface water pCO_2, although smaller than the projected increase in pCH_4, should not be neglected.

In contrast to the large influence of water temperature and DOC concentration in these predicted increases of surface water C-gas concentrations, the projected changes in water velocity had a negligible impact in every simulated scenario. The negative effect of water velocity on surface water pCO_2 and pCH_4 (Figure 2.5), was insufficient to offset the increase of pCO_2 and pCH_4 induced by rising water temperature and DOC concentrations (Table 2.4). In addition, the projected increase in water velocity was insignificant in terms of its impact on gas exchanges rates k_{600} (Table 2.4): A 130% increase of water velocity would be required to generate a significant increase in k_{600}. Such increase in water velocity is unlikely to occur in this region from the direct impact of climate change. Therefore, potential changes in fluvial C fluxes induced by hydrological alterations are minor and will be largely masked by changes induced by DOC loading and temperature (Table 2.4).

Table 2.4: Synthesis table of simulated changes in C fluxes parameters (pCO_2, pCH_4 and k_{600}) with standard errors (SE) for the year next 30 to 50 years and its resulting changes in average CO_2 and CH_4 fluxes (diffusive and non-diffusive) and total open water CO_2 and CH_4 emissions for the Abitibi and James Bay regions.

Parameter	Present	Scenario A	Scenario B	Scenario C	Scenario A		Scenario B		Scenario C	
	Median	Median	Median	Median	Change (%)	SE	Change (%)	SE	Change (%)	SE
pCO_2 (µatm)	2 456	2 506	2 599	2 799	2.0% ^{ns}	(±1)	5.8% ^{ns}	(±3)	14.0%	(±6)
pCH_4 (µatm)	725	972	1 117	1 390	34.1%	(±6)	54.0%	(±13)	91.8%	(±29)
k_{600} (m d^{-1})	0.85	0.85	0.86	0.87	-1.1% ^{ns}	(±0)	0.8% ^{ns}	(±0)	1.7% ^{ns}	(±0)
CO_2 departure (mg C/L)	1.14	1.10	1.14	1.23	-4.1% ^{ns}	(±2)	-0.6% ^{ns}	(±4)	7.7%	(±7)
CH_4 departure (mg C/L)	0.015	0.020	0.022	0.028	29.3%	(±6)	47.8%	(±13)	83.1%	(±28)
Gas Fluxes	**Average**	**Average**	**Average**	**Average**	**Change (%)**		**Change (%)**		**Change (%)**	
fCO_2 (mg C m^{-2} d^{-1})	977	927	980	1 071	-5.1% ^{ns}	(±1)	0.3% ^{ns}	(±4)	9.6%	(±8)
Diffusive fCH_4 (mg C m^{-2} d^{-1})	11.28	14.44	16.81	21,01	27.9%	(±6)	49.0%	(±14)	86.2%	(±29)
Non-Diffusive fCH_4 (mg C m^{-2} d^{-1})	23.90	30.77	34.66	41.87	28.8%	(±5)	45.1%	(±11)	75.2%	(±23)
Emissions	**Total**	**Total**	**Total**	**Total**	**Change (%)**		**Change (%)**		**Change (%)**	
CO_2 emission (tons of C)	34 932	34 781	37 761	46 173	-0.4% ^{ns}	(±2)	8.1% ^{ns}	(±6)	32.2%	(±15)
CH_4 emission (tons of C)	2 685	3 500	5 530	10 963	30.4%	(±5)	58.0%	(±12)	98.2%	(±27)
GHG emission (tons of C-eq.CO_2)	57 217	64 184	84 216	138 269	12.2%	(±3)	31.2%	(±8)	64.2%	(±20)
C emission (tons of C)	36 493	38 282	43 291	57 137	4.9%	(±2)	13.1%	(±5)	32.0%	(±11)

^{ns} : indicates non statistically significant changes.

2.6.5 Anticipated increase in fluvial GHG fluxes and emissions

We coupled the predicted increases in pCH_4, pCO_2 and k_{600} to estimate the ensuing changes in diffusive CO_2 and CH_4 fluxes using the Fick's law of gas diffusion (eq.1); we assumed an increase in atmospheric CO_2 and CH_4 concentration over the coming decades to 418 µatm and 3 µatm, respectively (Solomon *et al.*, 2007), and increase in average water temperature as described for each scenarios. In a previous study, we had calculated that non-diffusive CH_4 fluxes, resulting from surface water micro-bubbling evasion, was an important component of the total CH_4 fluxes to the atmosphere, which can be predicted in a function of surface water pCH_4 (Campeau *et al*, submitted). We used this empirical model to also quantify the potential increase of these non-diffusive CH_4 fluxes.

These calculations yield a large increase of both diffusive and non-diffusive CH_4 fluxes under scenarios of climate change, while CO_2 fluxes remain relatively stable (Table 2.4). We extrapolated these predicted future CO_2 and CH_4 fluxes to the entire fluvial network over an area of 44 182 km^2, and compared these with estimates of the current fluvial CO_2 and CH_4 gas emission for this same area, which we had developed previously (Campeau *et al.* submitted). In these calculations of future annual C-gas emissions, we also took into account the anticipated lengthening of the open water period, which will range between 6 to 18 days (from the current from 184 days) (Keyser *et al.*, 2000). This comparison between current and predicted future fluvial gas C-gas emissions for this entire region suggests that total C (CO_2 + CH_4

expressed as CO_2-equivalents) emissions may increase by 12 to 64%, largely driven by a disproportional increase in fluvial CH_4 emissions (30 to 98 %) relative to the increases in CO_2 emission (0 to 32%) (Table 2.4). The contribution of CH_4 to total GHG gas emissions (as CO_2-equivalents) will therefore also increase greatly, from the estimated current 36% (Campeau *et al*., submitted), to 46-67% (Table 2.4).

2.6.6 Conclusion and implications

There have been much recent research focusing on potential alterations of carbon biogeochemical processes in response to climate change, and there is ample evidence that key components of both the terrestrial and aquatic C systems are extremely sensitivity to projected thermal, physical or biological alterations. Fluvial networks have only recently been recognized as significant players in regional C sink/source budgets, and here we show that this regional role that these networks play will likely shift dramatically due to climate change. We have shown that despite the very different pathways involved, there is still an overall positive relationship between river pCO_2 and pCH_4, suggesting that they may share common drivers, at least at the scale of the whole fluvial network. We also show, however, that river CO_2 and CH_4 do not respond to these drivers in the same manner. In particular, fluvial CH_4 dynamics in these boreal networks appear to be much more temperature-sensitive than CO_2 dynamics, and also more sensitive to shifts in DOC. Our empirical models of surface water pCO_2, pCH_4 and gas exchange (k_{600}) based on predictive,

climate-sensitive variables (water temperature, velocity and DOC), suggest a large increase in total fluvial C-gas emissions under plausible scenarios of climate change, driven by a disproportional increase in the contribution of CH_4. Fluvial networks, which are an essential component of northern temperate and boreal landscapes, have traditionally not been considered significant CH_4 sources. We show here that this view greatly understates the role of these fluvial networks in terms of regional greenhouse gas dynamics, and emphasize that this role as "hot spots" of CH_4 emission to the atmosphere will likely be greatly amplified in the coming decades, under the effect on global warming.

CONCLUSION

Les résultats de mon projet de maitrise ont permis de faire la lumière sur des aspects méconnus des émissions aquatiques de gaz à effet de serre (GES) dans le biome boréal. Notre étude a démontré que les émissions de CH_4 provenant des réseaux fluviaux sont étonnamment importantes, contribuant à environ 36% des émissions de GES et de 30 à 60 % des émissions aquatiques totales de CH_4 provenant des deux régions sous étude. Une fraction démesurée des émissions fluviales de GES provient des plus petits ruisseaux d'ordre 1 (30% des émissions de l'ensemble du réseau fluvial) et lors de la fonte printanière (19% des émissions annuelles). Lors de l'élaboration de nos estimés régionaux d'émissions fluviales de GES, nous avons démontré que la pCO_2 et la pCH_4 suivaient des patrons similaires, diminuant en fonction de la longueur totale du ruisseau, ce qui semble cohérent au travers de divers types de paysages boréaux (Dawson *et al.*, 1995, Teodoru *et al.*, 2012, Wallin *et al.*, 2010). Nous avons constaté que le coefficient d'échange gazeux (k) variait en fonction de la vitesse d'écoulement de l'eau et qu'en conséquence, il augmentait au long du réseau fluvial, ce qui contraste largement avec les patrons établis dans des régions de plus forte topographie (Butman & Raymond, 2011, Raymond & Cole, 2001, Wallin *et al.*, 2011). Ces deux patrons pourront être utilisés pour l'élaboration d'estimés à grande échelle dans d'autres régions ou pour des usages comparatifs.

Ayant démontré l'importance des émissions fluviales de GES, nous avons également exploré la réponse potentielle de ces émissions face aux changements climatiques éminents dans la zone boréale. Nous avons identifié les facteurs de contrôle la pCO_2, la pCH_4 et le k parmi les propriétés des rivières les plus sensibles aux changements climatiques (thermiques, hydrologiques et biophysiques). De ce fait, nous avons démontré que dans un contexte où les changements climatiques causeront à la fois une augmentation de température de l'eau, de la vitesse d'écoulement et de concentration en DOC dans le réseau fluvial des régions sous étude, une augmentation significative de la pCO_2, pCH_4 et du k, donc des flux, seront à anticiper. Nous avons par la suite simulé l'impact des changements climatiques sur les flux de GES provenant du réseau fluvial par l'entremise de scénarios prédits et réalistes des changements climatiques projetés pour les deux régions sous étude. Ces simulations nous ont permis de déterminer qu'une augmentation considérable des émissions fluviales de GES (12 à 63%) au cours de prochaines décennies et pourrait survenir, considérant une hausse potentielle de 3-4 °C de la température atmosphérique estivale et une augmentation de ~12% du ruissèlement induit par l'augmentation des précipitations annuelles. Cette amplification des émissions de GES sera principalement causée par une augmentation marquée des émissions fluviales de CH_4 (30 à 98%) contrairement à une augmentation plutôt négligeable des émissions fluviales de CO_2 (0 à 28%). Selon ces scénarios, les émissions fluviales de CH_4 pourront contribuer à 46 à 67% des émissions fluviales de GES dans un avenir rapproché, une hausse de 27 à 86% de leur contribution actuelle estimée à 36%. Nous

avons également démontré que les processus biologiques aquatiques semblent contribuer de façon importante à l'approvisionnement en pCO_2 et pCH_4 dans les eaux de surface du réseau fluvial, suggérant que les changements climatiques influenceront les rivières et ruisseaux par l'entremise de changements dans la production aquatique de GES plutôt que par un changement dans l'apport en CO_2 et CH_4 provenant du milieu terrestre.

Ensemble, nos deux études ont démontré que les réseaux fluviaux boréaux sont des sources importantes de CH_4 atmosphérique, qui risquent de devenir d'autant plus importantes au cours des prochaines décennies dû à l'impact des changements climatiques. Il sera désormais important de déterminer si d'autres types d'écosystèmes boréaux, aquatiques et terrestres, répondront de façon similaire aux changements climatiques et ainsi affecteront de façon massive la balance de GES du biome boréal et le pool atmosphérique de GES. Un travail considérable doit également être effectué afin de faciliter l'intégration des émissions fluviales de GES dans le cycle du C, à l'échelle globale et du biome boréal. Pour parvenir à cette tâche, il nous faut tout d'abord faire la part entre la contribution du métabolisme fluvial (producteur de GES) et celle du métabolisme terrestre (exportateur de GES) aux émissions fluviales des GES actuels. De cette manière, il sera possible de discerner les différentes sources des émissions fluviales de GES, et ainsi d'identifier leur sensibilité aux changements climatiques dans le biome boréal et les mécanismes sous-jacents de la production de GES atmosphérique.

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